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Complex Halides of the Transition Metals. Part XVI.[1,2] The Octahalodirhenate(III) Anions. Reactions with the Bidentate Donors 1,2-Bis(diphenylphosphino)ethane and 2,2′-Bipyridyl

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The reaction of the salts $[Bu_4N]_2Re_2X_8$, where X = Cl or Br, with 1,2-bis(diphenylphosphino)ethane, abbreviated dppe, affords the halogen-bridged dimers $[ReX_3(dppe)]_2$ which contain magnetically dilute rhenium(III) centers. The properties of these complexes are contrasted with those found for the related 2,5-dithiahexane complexes $[ReX_3(DTH)]_2$ in which the dominant structural feature is a strong rhenium–rhenium bond. The reaction of $[Bu_4N]_2Re_2Cl_8$ with 2,2′-bipyridyl in n-butanol leads to the formation of unreduced and reduced phases, whose stoichiometries approach $[ReCl_3(bipy),3/2H_2O]_n$ and $[ReCl_{2.5}(bipy),3/8C_4H_9OH]_n$ respectively, but which do not structurally resemble the analogous complexes with dppe or DTH.

Introduction

The octachlorodirhenate(III) anion $Re_2Cl_8^{2-}$ has attracted considerable interest since it was first structurally characterized in 1965.[4] Its chemistry has been rationalized in terms of the presence of a strong rhenium–rhenium bond, formally of bond order four.[5] It reacts with bromide ion, thiocyanate ion, carboxylic acids, monodentate tertiary phosphines and certain sulfur donors to afford derivatives in which this metal–metal bond is retained.[5] It has also been found that the Re_2 unit persists in products formed from its polarographic reduction ($Re_2Cl_8^{3-}$ and $Re_2Cl_8^{4-}$),[6] reduction by tertiary phosphines ($Re_2Cl_4(PR_3)_4$)[7] and chlorine oxidation ($Re_2Cl_9^{2-}$)[8].

In making a comparison of the electronic absorption spectra of complexes of the type $[ReCl_3L]_n$, prepared from the $Re_2Cl_8^{2-}$ anion, we noted[9] that the spectrum of the complex with 1,2-bis(diphenylphosphino)ethane, abbreviated dppe, namely $[ReCl_3(dppe)]_n$, differed from that of other derivatives of this type. In an effort to explain this spectral difference we have explored the chemistry of this complex. Related studies have also been carried out on the species formed from the reaction between the $Re_2Cl_8^{2-}$ anion and the bidentate nitrogen donor 2,2′-bipyridyl. We now report in full the results of this study, some preliminary details of which have recently been presented.[1]

Experimental

Organic reagents and solvents were obtained from commercial sources and were used as received unless stated otherwise. The salts $[Bu_4N]_2Re_2X_8$, where X = Cl or Br, and their derivatives with 2,5-dithiahexane $[ReX_3(DTH)]_2$, were prepared by literature methods.[9,10]

All reactions were carried out in a nitrogen atmosphere unless otherwise stated.

The Reaction of $[Bu_4N]_2Re_2Cl_8$ with 1,2-Bis(diphenylphosphino)ethane

$[Bu_4N]_2Re_2Cl_8$ (1.5 g) was reacted with 1.15 g of dppe dissolved in 140 ml of acetonitrile. The reaction mixture was stirred for 30 min at room temperature to produce a green solution and a magenta-colored precipitate. The precipitate (1.03 g) was filtered from the solution and was washed with 30 ml of acetonitrile and 30 ml of diethylether. The precipitate was air-dried for about 20 min. Yield, 57%. *Anal.* Calcd. for $C_{26}H_{24}Cl_3P_2Re$: C, 45.2; H, 3.5; P, 9.0; Cl, 15.4. Found: C, 45.2; H, 3.4; P, 8.7; Cl, 15.2.

The Reaction of $[Bu_4N]_2Re_2Br_8$ with 1,2-Bis(diphenylphosphino)ethane

$[Bu_4N]_2Re_2Br_8$ (0.071 g) was dissolved in an acetonitrile solution of dppe (0.066 g in 10 ml) and stirred for 1 hour. A dark green powder precipitated and was removed by filtration, washed with acetonitrile and diethylether and air-dried. Yield, 84%. *Anal.* Calcd. for $C_{26}H_{24}Br_3P_2Re$: C, 37.9; H, 2.9; Br, 29.1. Found: C, 37.7; H, 3.2; Br, 29.3.

The reaction was repeated several times and in every instance the results of microanalysis of the dark green product indicated that it had a stoichiometry somewhere between $[ReBr_3(dppe)]_n$ and $[ReBr_{2.5}(dppe)]_n$. *Anal.* Calcd. for $C_{26}H_{24}Br_{2.5}P_2Re$: C, 39.8; H, 3.1;

Br, 25.5. Found for separate samples: C, 39.0, 37.9; H, 3.1, 3.15; Br, 25.8, 26.2.

All these products exhibited identical spectral properties and reactivity patterns, so the bromine deficient materials are probably best considered to be $[ReBr_3(dppe)]_n$ contaminated by variable quantities of a reduced phase. For convenience these products are formulated as $[ReBr_3(dppe)]_n$ in all subsequent discussions.

The Reaction of $[Bu_4N]_2Re_2Cl_8$ *with 2,2'-Bipyridyl*

A mixture of $[Bu_4N]_2Re_2Cl_8$(1.0 g) and 2,2'-bipyridyl (0.41 g) was dissolved in refluxing n-butanol and reflux continued for 16 min. The reaction mixture was then cooled to room temperature, the grey-black microcrystalline insoluble product (0.58 g) filtered off and washed with n-butanol (5 × 15 ml) and then diethylether. It was air-dried for 1 hr and stored in a desiccator over $CaCl_2$. This product analyzed closely for a complex of stoichiometry $ReCl_3(bipy)\cdot 3/2H_2O$. *Anal.* Calcd. for $C_{10}H_{11}Cl_3N_2O_{1.5}Re$: C, 25.2; H, 2.3; N, 5.9; Cl, 22.4. Found: C, 25.2; H, 2.2; N, 5.9; Cl, 22.2.

The water in this product presumably arises from the incompletely dried n-butanol. Reaction times appreciably shorter than 16 min may lead to some unreacted $[Bu_4N]_2Re_2Cl_8$, while with longer reaction times reduction may begin to occur (see below).

$[Bu_4N]_2Re_2Cl_8$ (2.0 g) and 2,2'-bipyridyl (2.7 g) were dissolved in 120 ml n-butanol and the reaction mixture refluxed for 48 hr. The reaction flask was cooled to room temperature, the brown insoluble product filtered off and the deep blue, viscous filtrate discarded. The product (0.49 g) was washed with n-butanol (7 × 15 ml) and generously with anhydrous ether. It was then *air-dried* for 30 min and stored in a desiccator over $CaCl_2$. This brown product had a stoichiometry very close to $ReCl_{2.5}(bipy)\cdot 3/8C_4H_9OH$. *Anal.* Calcd. for $C_{11.5}H_{11.75}Cl_{2.5}N_2O_{0.375}Re$: C, 30.1; H, 2.6; N, 6.1; Cl, 19.3. Found: C, 30.35; H, 2.3; N, 6.7; Cl, 19.2.

Heating either of these compounds *in vacuo* at 100° C for periods of up to 20 hr. did not completely remove water or n-butanol from them. The use of other solvents for the reactions resulted in the 2,2'-bipyridinium ion being present[11] in the products when ethanol or n-propanol were used, and the presence of an imine contaminant when acetonitrile was used.

In the present study we also investigated the reaction of $[Bu_4N]_2Re_2Br_8$ with 2,2'-bipyridyl in a variety of alcohols and of $[Bu_4N]_2Re_2Cl_8$ with 2,2',2''-terpyridyl, but in none of these systems were we able to obtain reproducible or readily characterizable products and accordingly these reactions were not pursued further.

The Reaction of $[ReX_3(dppe)]_n$ *with Acetic Acid–Acetic Anhydride*

$[ReCl_3(dppe)]_n$ (0.10 g) was combined with 6 ml of acetic acid and 2 ml of acetic anhydride and the reaction mixture heated on a steam bath for 3 hr. After this time the orange product which had precipitated from the orange-brown colored solution was removed by filtration. Yield, 17%. The filtrate was replaced on the steam bath and heated for an additional 5 hr, during which time a green crystalline product separated. Yield, 27%. Both insoluble products were washed with absolute ethanol and diethylether prior to drying.

The microanalysis of the orange crystals approached that expected for $ReCl_4$dppe. *Anal.* Calcd. for $C_{26}H_{24}Cl_4P_2Re$: C, 42.99; H, 3.36; Cl, 19.52. Found: C, 42.09; H, 3.29; Cl, 18.97. In some cases the orange product was contaminated by small amounts of $Re_2(O_2CCH_3)_4Cl_2$ which were detected by means of X-ray powder photography and infrared spectroscopy. This impurity, due to its insolubility, could be removed by recrystallizing the orange product from acetonitrile.

The microanalysis of the green product was somewhat variable but approximated to the stoichiometry $ReOCl_3(dppeO_2)$. *Anal.* Calcd. for $C_{26}H_{24}Cl_3O_3P_2Re$: C, 42.3; H, 3.3; Cl, 14.4. Found for separate samples: C, 43.6, 42.5; H, 3.4, 3.3; Cl, 15.7, 15.2.

These two complexes formed essentially non-conducting solutions in acetonitrile: Λ_m (orange) = 5.5 mho cm^2 (c = 1.2×10^{-3} *M*); Λ_m (green) = 9.6 mho cm^2 (c = 4.2×10^{-4} *M*).

The reaction of a sample of $ReOCl_3(dppe)$, prepared by the method of Chatt and Rowe,[12] with acetic acid and acetic anhydride yielded two different products. The first of these, resulting from steam heating, was a crop of blue crystals that were identified by infrared and electronic absorption spectroscopy to be the recrystallized starting material. The second product was an orange powder resulting from a rapid reflux maintained using a heating mantle. This product was identified as the tetraacetate, $Re_2(O_2CCH_3)_4Cl_2$, by infrared and electronic absorption spectroscopy. In neither instance was there evidence for the formation of green $ReOCl_3(dppeO_2)$.

A similar reaction of $[ReCl_3(dppe)]_n$ with refluxing acetic acid and acetic anhydride, using a heating mantle instead of steam heating, yielded an orange product that was largely composed of the tetraacetate.

The reaction of $[ReBr_3(dppe)]_n$ with acetic acid–acetic anhydride, in a manner similar to that already described for $[ReCl_3(dppe)]_n$, afforded a redbrown solution from which red crystals of $ReBr_4(dppe)$ were obtained after 7 hr. Yield, 52%. *Anal.* Calcd. for $C_{26}H_{24}Br_4P_2Re$: C, 34.5; H, 2.7; P, 6.8. Found: C, 35.15; H, 3.0; P, 7.0.

The Reaction of $[ReCl_3(dppe)]_n$ *with Triphenylphosphine*

The reaction of $[ReCl_3(dppe)]_n$ with triphenylphosphine in refluxing acetonitrile did not afford green $[ReCl_3(PPh_3)]_2$ and so was not pursued further.

The Reaction of $[ReX_3(dppe)]_n$ with Halocarbons

A suspension of $[ReCl_3(dppe)]_n$ (0.4 g) in a mixture of 50 ml of carbon tetrachloride and 50 ml of dichloromethane was refluxed on a steam bath for 1 hr, to produce a clear yellow solution. The solution was evaporated to dryness by suction and gentle heating to yield a yellow crystalline product in quantitative yield. The product was washed with 50 ml of diethylether and air-dried. Microanalysis showed the compound to be $ReCl_4(dppe) \cdot 3/4CCl_4$. *Anal.* Calcd. for $C_{26.75}H_{24}Cl_7P_2Re$: C, 38.2; H, 2.9; P, 7.4; Cl, 29.5. Found: C, 37.1; H, 2.4; P, 7.4; Cl, 29.4.

This complex was a non-electrolyte in acetonitrile (Λ_m = 2.4 mho cm^2 for c = $1.2 \times 10^{-3}M$) and possessed a room-temperature magnetic moment of 3.26 B.M.

The corresponding solvates $ReCl_4(dppe) \cdot CCl_3CN$, $ReCl_4(dppe) \cdot CCl_3NO_2$, $ReCl_4(dppe) \cdot 3/4Cl_3CCH_3$ and $ReBr_4(dppe) \cdot 1/2CBr_4$ were prepared in quantitative yield by a very similar procedure to that described for $ReCl_4(dppe) \cdot 3/4CCl_4$. Microanalytical data for these products are as follows:

Calcd. for $C_{28}H_{24}Cl_7NP_2Re$: C, 38.6; H, 2.8; N, 1.6; Cl, 28.5. Found: C, 37.6; H, 2.75; N, 1.9; Cl, 29.8. Calcd. for $C_{27}H_{24}Cl_7NO_2P_2Re$: C, 36.6; H, 2.7; N, 1.6; Cl, 27.9. Found: C, 36.3; H, 2.6; N, 1.5; Cl, 27.6. Calcd. for $C_{27.5}H_{26.3}Cl_{6.25}P_2Re$: C, 40,0; H, 3.2; Cl, 26.8. Found: C, 40.1; H, 3.2; Cl, 26.2. Calcd. for $C_{26.5}H_{24}Br_6P_2Re$: C, 29.3; H, 2.3; Br, 45.0. Found: C, 29.25; H, 2.2; Br, 43.9.

Oxidation of $[ReX_3(dppe)]_n$ with freshly purified, deoxygenated CHX_3 yielded the unsolvated complexes $ReX_4(dppe)$. *Anal.* Calcd. for $C_{26}H_{24}Cl_4P_2Re$: C, 43.0; H, 3.4; Cl, 19.5. Found: C, 42.3; H, 3.3; Cl, 18.65. Calcd. for $C_{26}H_{24}Br_4P_2Re$: C, 34.5; H, 2.7; Br, 35.3. Found: C, 33.35; H, 3.05; Br, 35.5.

After dissolving a sample of $ReCl_4(dppe)$ $3/4CCl_4$ (0.33 g) in 100 ml of acetonitrile with steam heating, the solvent was evaporated by further heating. The yellow product that remained was washed with 50 ml of diethylether and dried *in vacuo* at room temperature. *Anal.* Calcd. for $C_{26}H_{24}Cl_4P_2Re$: C, 43.0; H, 3.4; Cl, 19.5. Found: C, 42.2; H, 3.2; Cl, 19.9.

Treatment of the other chlorocarbon solvates in a similar fashion also afforded the unsolvated complex $ReCl_4(dppe)$.

The Reactions of $[ReCl_3(dppe) \cdot 3/2H_2O]_n$ and $[ReCl_{2.5}(dpp) \cdot 3/8C_4H_9OH]_n$

The reactions of these complexes with methanol–HCl (4 : 1 v/v), acetonitrile solutions of triphenylphosphine, mixed carbon tetrachloride–dichloromethane (1 : 1 v/v) and solutions of tetraphenylarsonium chloride in carbon tetrachloride–dichloromethane under reflux conditions, did not yield identifiable rhenium(IV) or monomeric or dinuclear rhenium(III) species.

The Reaction of $[ReX_3(DTH)]_2$ with Acetic Acid–Acetic Anhydride

A sample of $[ReCl_3(DTH)]_2$ (0.07 g) was ground to a fine powder and placed in a round-bottom flask with 8 ml of acetic acid and 2 ml of acetic anhydride. The reaction mixture was heated for 20 min and the resulting orange-brown, insoluble acetate $Re_2(O_2CCH_3)_4Cl_2$ (0.051 g) filtered off and washed with acetic acid–acetic anhydride (4 : 1 v/v), ethanol and diethylether. Yield, 89%. *Anal.* Calcd. for $C_4H_{12}Cl_2O_8Re_2$: C, 14.1; H, 1.8. Found: C, 14.1; H, 1.9.

The infrared spectrum of this orange-brown product contained bands attributable only to the authentic tetraacetate, $Re_2(O_2CCH_3)_4Cl_2$.[13]

A similar reaction of $[ReBr_3(DTH)]_2$ with a 4 : 1 v/v mixture of acetic acid and acetic anhydride yielded a brown, insoluble precipitate (0.04 g) which was filtered from the solution and washed with acetic acid–acetic anhydride (4 : 1 v/v), absolute ethanol and diethylether. Yield, 95%. *Anal.* Calcd. for $C_4H_{12}Br_2O_8Re_2$: C, 12.5; H, 1.6; Br, 20.8. Found: C, 12.7; H, 1.75; Br, 20.8.

The infrared and electronic spectra of the brown product contained absorption bands which were attributable only to authentic $Re_2(CH_3CO_2)_4Br_2$.[13]

The Reaction of $[ReX_3(DTH)]_2$ with Triphenylphosphine

$[ReCl_3(DTH)]_2$ (0.06 g) was reacted with an excess of triphenylphosphine (0.20 g) in 10 ml of acetonitrile. The reaction mixture was refluxed on a steam bath for 3 hr, at which time, the green insoluble complex $[ReCl_3(PPh_3)]_2$ that had formed was removed by filtration. The product (0.064 g) was washed with absolute ethanol and diethylether. Yield, 80%. *Anal.* Calcd. for $C_{18}H_{15}PReCl_3$: C, 38.95; H, 2.7; P, 5.6; Cl, 19.2. Found: C, 38.6; H, 2.7; P, 5.6; Cl, 19.5.

The bromide complex $[ReBr_3(DTH)]_2$ was readily converted to brown $[ReBr_3(PPh_3)]_2$ by a related procedure to that described for $[ReCl_3(DTH)]_2$.

Both products had infrared and electronic absorption spectra identical with those of authentic samples of these complexes prepared from the reaction of $[Bu_4N]_2Re_2X_8$ with triphenylphosphine.[10]

The Reaction of $[ReX_3(DTH)]_2$ with Halocarbons

The complexes $[ReX_3(DTH)]_2$ showed little reactivity towards the refluxing halocarbons CCl_4, CCl_3NO_2 and CBr_4 even when reacted for prolonged periods.

Physical Measurements

Infrared spectra were recorded as nujol mulls on a Beckman IR-12 spectrophotometer. Diffuse reflectance (D.R.) and Nujol Mull (N.M.) electronic spectra were recorded using Cary 14 and Beckman DU-2 spectrophotometers. Magnetic moments were determined by the Gouy method using $Hg[Co(SCN)_4]$ as the calibrant. Corrections for the ligand diamagnetism were estimated from Pascal's Constants. Conductance measurements were made with a Model RC 16B2 conductivity bridge from Industrial Instruments Inc. X-Ray photoelectron spectra were recorded as described elsewhere.[14,15]

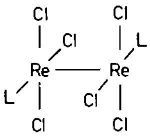
Analytical Procedures

Elemental microanalyses were performed by Dr. C. S. Yeh of the microanalytical laboratory of this department or by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Results and Discussion

1,2-Bis(diphenylphosphino)ethane

Under our experimental reaction conditions the yield of the magenta colored complex $[ReCl_3(dppe)]_n$, first reported by Cotton *et al*[10] to be formed from the reaction between $[Bu_4N]_2Re_2Cl_8$ and dppe in acetonitrile, did not exceed ~60%. Prolonged reflux of the green reaction filtrate afforded a very low yield (~6%) of a black crystalline compound which appears to be of stoichiometry $[ReCl_2(dppe)]_n$ but which we have not yet adequately characterized. This reaction sequence formally resembles that previously found for the reaction between $[Bu_4N]_2Re_2Cl_8$ and 2,5-dithiahexane ($CH_3SCH_2CH_2SCH_3$, abbreviated DTH), namely initial formation of metal–metal bonded dimer $[ReCl_3(DTH)]_2$,[9] followed by conversion to a lower oxidation state complex.[9,16] Although the complete structural details of $[ReCl_3(DTH)]_2$ are not yet known it is believed to have a structure related to that of the phosphine complex $[ReCl_3(PEt_3)]_2$[17] in view of the striking similarity of its electronic absorption spectrum to that of the $Re_2Cl_8^{2-}$ anion and other complexes of the type $[ReCl_3(L)]_2$[9] (see structure I). Suitable single crystals of the dppe complex were grown from an acetonitrile solution and a single crystal X-ray analysis has shown this species to be the acetonitrile solvate of the centrosymmetric chlorine-bridged dimer $[ReCl_3dppe]_2$ (structure II).[1]



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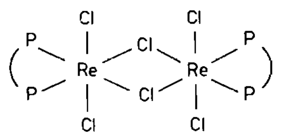


II

The possibility of a structural similarity between the complexes with dppe and DTH was quickly dispelled upon considering the physical properties and chemical reactivities of these two systems. We found that when the complex $[ReCl_3(DTH)]_2$, and its bromide analog, were reacted with triphenylphosphine and acetic acid–acetic anhydride, they were converted in high yield (>70%) to the known complexes $[ReX_3(PPh_3)]_2$ and $Re_2(O_2CCH_3)_4X_2$, species which are readily formed directly from the $Re_2X_8^{2-}$ anions.[10,13] This behavior is convincing evidence that the complexes $[ReX_3(DTH)]_2$ do indeed possess a metal–metal bonded structure related to that of I.

In contrast to this, the complex $[ReCl_3(dppe)]_2$ reacted with triphenylphosphine and acetic acid–acetic anhydride in a quite different fashion. While an identifiable product was not isolated from the reaction with triphenylphosphine, the green dimer $[ReCl_3(PPh_3)]_2$[10] was not formed. When it was reacted with acetic acid–acetic anhydride at 90° C in a nitrogen atmosphere a complex oxidation reaction occurred. Orange crystals of the rhenium(IV) complex $ReCl_4(dppe)$, green crystals of the rhenium(V) complex $ReOCl_3(dppeO_2)$ and a trace of the acetate $Re_2(O_2CCH_3)_4Cl_2$ were isolated. This oxidation must involve oxygen-abstraction from the solvent system, but further details of the mechanism are at present unknown. The yield of the latter complex increased substantially when the reaction was carried out under vigorous reflux conditions (~120° C), but it is only a minor byproduct under the experimental conditions which we used in comparing the reactivities of $[ReCl_3(DTH)]_2$ and $[ReCl_3(dppe)]_2$.

$ReCl_4(dppe)$ exhibited the typical spectral and magnetic properties of a complex of rhenium(IV) and was found to be identical with samples of this complex prepared by an alternative route (see later). The green rhenium(V) complex, which was difficult to isolate very pure, exhibited characteristic intense infrared absorption bands at 984 cm^{-1} [$\nu(Re{=}O)$] and 1086 and 1134 cm^{-1} [$\nu(P = O)$],[18] which appear to confirm the identity of this product. Both derivatives formed essentially non-conducting solutions in acetonitrile. Since we observed that $ReCl_4(dppe)$ is formed before oxidation to green $ReOCl_3(dppeO_2)$ occurs, this reaction appears to proceed through the sequential one electron oxidations $Re^{III} \rightarrow Re^{IV} \rightarrow Re^{V}$. Although it seemed reasonable that the complex $ReOCl_3(dppe)$[12] would be a precursor in the formation of $ReOCl_3(dppeO_2)$, the reaction between $ReOCl_3(dppe)$ and acetic acid–acetic anhydride did not proceed in this fashion. Reaction at ~90° C simply affected the recrystallization of the starting material as large blue crystals whereas vigorous reflux (~120° C) yielded the tetraacetate $Re_2(O_2CCH_3)_4Cl_2$. Indeed, reaction of $[ReCl_3(dppe)]_2$ with acetic acid–acetic anhydride under these same vigorous reflux conditions also yielded significant quantities of the tetraacetate, so that this is the preferred reaction product under these forcing conditions, irrespective of whether the starting rhenium chloride complex is mononuclear or a metal–metal bonded dimer or even trimer (*e.g.* Re_3Cl_9).[19]

Another striking difference between the reactivities of $[ReX_3(DTH)]_2$ and $[ReCl_3(dppe)]_2$ involved their behavior towards chlorocarbons of the type CCl_3X, where X = Cl, CN, NO_2, CH_3 or H. Whereas the 2,5-dithiahexane complexes did not appear to react with these reagents under our experimental conditions, the complex $[ReCl_3(dppe)]_2$ was smoothly oxidized, in quantitative yield, to solvates of the orange colored rhenium(IV) complex $ReCl_4(dppe) \cdot xCCl_3X$, where x = 1 for X = CN or NO_2, 3/4 for X = Cl or CH_3 and 0 for X = H.[20] The mass spectra of these complexes showed that prior to their complete thermal decomposition the only volatile portions were the CCl_3X molecules. Dissolution of these solvates in acetonitrile followed by evaporation of the solutions to dryness afforded the unsolvated complex $ReCl_4(dppe)$. The solvated complexes could be reconstituted by redissolving $ReCl_4(dppe)$ in the appropriate chlorocarbon. The electronic absorption spectra of these complexes were characteristic of octahedral rhenium(IV) species[21,22] and showed a very close correspondence to the related spectra of species such as $ReCl_6^{2-}$ and $[ReCl_5(CH_3CN)]^-$.[21] These data together with other pertinent and characteristic spectral properties are presented in Table I.

The reaction between $[Bu_4N]_2Re_2Br_8$ and dppe in acetonitrile differed from the reaction of the related chloride in that it was difficult to isolate $[ReBr_3(dppe)]_2$ free from reduced rhenium species. However, that this product was structurally related to $[ReCl_3(dppe)]_2$ was clearly shown by its reactivity patterns. When it was refluxed with acetic acid–acetic anhydride, red $ReBr_4(dppe)$ was isolated in good yield. While no higher oxidation state species were isolated, this behavior resembles that noted for $[ReCl_3(dppe)]_2$. By direct analogy with the latter complex, $[ReBr_3(dppe)]_2$ was oxidized by carbon tetrabromide and bromoform in quantitative yield to $ReBr_4(dppe) \cdot 1/2CBr_4$ and $ReBr_4(dppe)$, respectively. These products are authentic complexes of rhenium(IV) (Table I).

The magnetic and spectral properties of $[ReCl_3(dppe)]_2$ further distinguish it from $[ReCl_3(DTH)]_2$. It has a room-temperature magnetic moment of 2.05 B.M. (per monomeric formula unit), a value which is consistent with magnetically dilute rhenium(III) centers.[23,24] The solid-state electronic spectrum of this complex appears to be characteristic of magnetically dilute rhenium(III) and exhibits very prominent low energy absorptions at ~5,700 and 9,000 cm^{-1} (Table II). This low energy spectrum is rather similar to that exhibited by the $t_{2g}^4e_g^0$ $OsCl_6^{2-}$ anion,[25] in which a band at 5,200 cm^{-1} is assigned to the spin-allowed

TABLE I. Spectral Properties of Rhenium(IV) Complexes from the Oxidation of $[ReX_3(dppe)]_n$.

Complex	Medium	Electronic Absorption Maxima $\times 10^{-3}$ cm^{-1}						Infrared Spectra	
		$^4A_{1g} \rightarrow {}^2T_{1g}(\Gamma_8)$	$^2E_g(\Gamma_8)$	$^2T_{1g}(\Gamma_6)$	$^2T_{2g}(\Gamma_7)$	$^2T_{2g}(\Gamma_8)$		ν(C–X) of halocarbons	ν(Re–X)
$ReCl_4(dppe) \cdot 3/4CCl_4$	D.R.	~7.0w, br; 7.3w;	7.9mw;	8.2mw;	13.0m;	15.6m;	21.1s	790m	–
	N.M.	6.85sh; 7.3w;	7.9w;	8.25w;	13.0m;	15.55m;	21.1s		
$ReCl_4(dppe) \cdot CCl_3CN$	D.R.	7.1m; 7.4m;	8.0sh;	8.3m;	~12.6m;	15.6m;	21.0s	790s	–
$ReCl_4(dppe) \cdot CCl_3NO_2$	N.M.	7.1m; 7.3m;	7.9m;	8.3m;	13.0m;	15.7m;	21.0s	a	–
$ReCl_4(dppe) \cdot 3/4CCl_3CH_3$	N.M.	6.8w; 7.3m;	7.85m;	8.25m;	13.5m;	16.1m;	21.2s	b	–
$ReCl_4(dppe)$	D.R.	~7.1mw, vbr;	7.9mw;	8.25mw;	12.9m;	15.6m;	21.1s	–	347sh; 328s; 302vs
	N.M.	6.8w; 7.3w;	7.9w;	8.3w;	13.1m;	15.6m;	21.1s		
$ReBr_4(dppe) \cdot 1/2CBr_4$	D.R.	6.4w?; 7.1mw;	7.5sh;	7.8m;	11.5m;	12.5m;	18.45s, br	c	–
$ReBr_4(dppe)$	N.M.	6.4m; ~7.1mw, br;	7.5sh;	7.8m;	11.7m;	12.5m;	19.1s	–	231s

[a] ν(C–Cl) obscured by dppe absorptions but other CCl_3NO_2 vibrational frequencies clearly observed at 675 sh; 847w; 858m; 903m and 1603s (see J. Mason, J. Dunderdale and A. H. Castelli, *J. Chem. Soc.*, 1959, 2014). [b] ν(C–Cl)expected close to 725 cm^{-1} (see D. C. Smith, G. M. Brown, J. R. Nielsen, R. M. Smith and C. Y. Liang, *J. Chem. Phys.*, 1952, *20*, 473) but obscured by dppe absorptions. [c] ν(C–Br) expected close to 672 cm^{-1} (see S. Abramowitz and R. P. Bauman, *Spectrochim Acta.*, 1961, *17*, 125) but obscured by dppe absorptions.

TABLE II. Complexes from the Reaction of $Re_2X_8^{2-}$ with 1,2-Bis(diphenylphosphino)ethane and 2,2′-Bipyridyl.

Complex		Electronic Absorption Maxima $\times 10^{-3}$ cm^{-1}	Low Frequency I.R. Spectra[a]
$[ReCl_3(dppe)]_2$	D.R.	5.75s; 8.7m; 10.5sh; 18.7s; ~21.7s	*330s; 260m–s;* 230m–w
	N.M.	5.7s; 9.7m; ~10.7sh; 18.4sh; 22.2sh	
$[ReBr_3(dppe)]_2$	D.R.	5.6s; ~7.8sh; 8.55m; 10.3w; ~17.7sh, br	327m–w; 287vw; *241s*
$[ReCl_3(bipy) \cdot 3/2H_2O]_n$	D.R.	~13.3sh; ~14.6?sh; ~15.6sh; 17.0sh; 17.9s	*335vs;* 279vw?; ~232m–w
	N.M.	6.6m,br; ~13.3sh; 17.9s	
$[ReCl_{2.5}(bipy) \cdot 3/8C_4H_9OH]_n$	D.R.	~12.5sh; ~17.9sh; ~21.3sh	*324sh; 306s;* 280vw; 228w
	N.M.	5.7m,br; ~17.9sh; ~21.3sh	
$Re_2Cl_5(DTH)_2$[b]	D.R.	9.8; 13.3; 16.4	*341sh; 331vs; 318s;* 279w; 254m–w; 232m; ~210w

[a] ν(Re–X) modes are in italics. [b] I.R. frequencies for this complex are given in this table since our data differ somewhat from that reported in the literature (see reference 27). The sample used in the present spectral study was that from which crystals were taken for the single crystal X-ray structure analysis (see reference 16).

$^3T_{1g} \rightarrow {}^3T_{1g}$ transition and the weaker feature at 11,300 cm^{-1} to a composite spin-forbidden $^3T_{1g} \rightarrow {}^1T_{2g}, {}^1E_g$ transition. Consistent with this, we note that the band at 5,700 cm^{-1} in the spectrum of $[ReCl_3(dppe)]_2$ is sharper and more intense than the broad structured feature centered at ~9,000 cm^{-1}. As expected, the bromide complex $[ReBr_3(dppe)]_2$ exhibits an electronic absorption spectrum (Table II) which is strikingly similar to that of its chloride analog.

We have previously noted[2, 26] that for complexes of rhenium(IV), (III) and (II), differences in coordination number and ligand electronegativity and π-acceptor ability rarely permit a simple correlation between rhenium 4*f* electron binding energies and the metal oxidation state. However, the complexes $[ReCl_3(dppe)]_2$ and $ReCl_4(dppe)$ discussed herein both contain the $[ReCl_4(dppe)]$ structural unit and it was of particular interest to see whether the rhenium 4*f* binding energies would be significantly different. As can be seen from the data in Table III, the rhenium(III) complex has much lower values for its Re $4f_{5/2,7/2}$ binding energies than the rhenium(IV) complex, consistent with its lower oxidation state. These systems constitute one of the relatively few examples where metal binding energy shifts in *neutral* metal complexes can usefully be compared with the metal centers in closely similar environments.

2,2′-Bipyridyl

Although there is one literature report which deals with the reaction of the $Re_2Cl_8^{2-}$ anion with 2,2′-bipyridyl,[9] this earlier preliminary study afforded little definitive information on the structure of this system and in particular its relationship, if any, to products from the reaction of this dianion with other donor molecules. We are now able to clarify somewhat the nature of this system. The reflux reaction of $[Bu_4N]_2Re_2Cl_8$ with 2,2′-bipyridyl in n-butanol initially yields a grey-black insoluble product of empirical formula $ReCl_3(bipy) \cdot 3/2H_2O$ after a reaction time of *ca.* 15 minutes. The presence of water is not unexpected since the n-butanol solvent was not scrupulously dried prior to use. This compound is apparently the same as the dark blue material previously formulated by us[9] as $ReCl_3(bipy)$. With an increase in reaction time and increase in the $[Bu_4N]_2Re_2Cl_8$: 2,2′-bipyridyl mole ratio from 1 : 3 to 1 : 10, reduction occurs and a brown product of stoichiometry close to $ReCl_{2.5}(bipy) \cdot 3/8C_4H_9OH$ is obtained.

The infrared spectra of $[ReCl_3(bipy) \cdot 3/2H_2O]_n$ and $[ReCl_{2.5}(bipy) \cdot 3/8C_4H_9OH]_n$ were almost identical in

TABLE III. X-Ray Photoelectron Spectra.[a, b]

Complex	Re		Cl		Nls	Cls
	$4f_{5/2}$	$4f_{7/2}$	$2p_{1/2}$	$2p_{3/2}$		
$ReCl_4(dppe) \cdot 3/4CCl_4$	45.3(1.3)	42.8(1.4)	199.9(1.3)	198.3(1.15)	–	–
$ReCl_4(dppe)$	45.4(1.5)	43.1(1.4)	199.8(1.6)	198.3(1.4)	–	–
$[ReCl_3(dppe)]_2$	43.3(1.6)	41.0(1.6)	c	197.6	–	–
$[ReCl_3(bipy) \cdot 3/2H_2O]_n$	44.7(2.2)	42.4(2.2)	199.6(1.7)	198.1(1.5)	399.7	284.6
$[ReCl_{2.5}(bipy) \cdot 3/8C_4H_9OH]_n$	44.2(2.2)	41.9(1.9)	199.5(1.5)	198.1(1.8)	400.0	284.8

[a] Binding energies are quoted relative to a value of 284.0eV for the C 1*s* binding energy of graphite. [b] FWHM values are given in parentheses. [c] The Cl $2p_{1/2}$ component was not sufficiently well resolved to enable its position to be accurately located.

the 4000–400 cm^{-1} region and showed bands characteristic only of coordinated 2,2′-bipyridyl. There was no spectral evidence for significant contamination by Re=O, ReO_4^- or 2,2′-bipyridinium species. The $bipyH^+$ cation is known to be present in the products resulting from the reduction of Re_3Cl_9 by 2,2′-bipyridyl,[11] so in the reaction leading to $[ReCl_{2.5}(bipy) \cdot 3/8C_4H_9OH]_n$, any organic oxidation by-products clearly remain in solution and do not contaminate the insoluble metal containing species. The low frequency infrared spectra of $[ReCl_3(bipy) \cdot 3/2H_2O]_n$, $[ReCl_3(dppe)]_2$ and $[ReCl_3(DTH)]_2$ (see Table II and reference 27) are sufficiently different that it is unlikely that any of these complexes have closely similar structures. In accord with this we found that the complex with 2,2′bipyridyl is neither oxidized by the chlorocarbons CCl_4/CH_2Cl_2 or CCl_3CH_3, to produce the rhenium(IV) complex $ReCl_4(bipy)$, nor does it react with methanol–HCl or an acetonitrile solution of triphenylphosphine to afford the species $[bipyH]_2Re_2Cl_8$[9] or $[ReCl_3(PPh_3)]_2$.[10] The reduced phase $[ReCl_{2.5}(bipy) \cdot 3/8C_4H_9OH]_n$ has a low frequency i.r. spectrum which in no way resembles that of the non-centrosymmetric dimer $Re_2Cl_5(DTH)_2$.[9,16] The ν(Re–Cl) patterns for these two complexes are quite different and in contrast to the DTH complex, $[ReCl_{2.5}(bipy) \cdot 3/8C_4H_9OH]_n$ does not exhibit an infrared active ν(Re–Re) mode close to 259 cm^{-1}.[27] From these infrared spectral studies it is also apparent (Table II) that this reduced phase with 2,2′-bipyridyl does not contain any unreduced $[ReCl_3(bipy)]_n$.

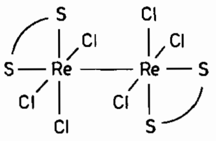
Both bipyridyl complexes are insoluble in all except strongly coordinating solvents and even then their solubilities are extremely low. A brown solution of $[ReCl_3(bipy) \cdot 3/2H_2O]_n$ in dimethylformamide ($9.6 \times 10^{-4}M$) had a molar conductance of 27 mho cm^2, a value which is lower than that expected for a 1:1 electrolyte in this solvent.[28]

The electronic absorption spectrum of $[ReCl_3(bipy) \cdot 3/8C_4H_9OH]_n$ does not resemble that expected for magnetically dilute rhenium(III) [*e.g.* $[ReCl_3(dppe)]_2$ in Table II] or diamagnetic dinuclear metal–metal bonded complexes of the type $[ReCl_3L]_2$ [*e.g.* $[ReCl_3(DTH)]_2$].[9] Accordingly, it would seem to have a structure quite different from either of these, and its room-temperature magnetic moment (1.36 B.M. at 297° K) adds credence to this suggestion. This magnetic moment is significantly lower than the value normally encountered[23,24] for magnetically dilute rhenium(III) so that a structure in which some degree of metal–metal interaction occurs is quite likely.

If we assume a dimeric formulation for the reduced phase $[ReCl_{2.5}(bipy) \cdot 3/8C_4H_9OH]_n$, the experimentally determined room temperature magnetic moment is 1.96 B.M. per dimer. Such a value is consistent with the presence of one unpaired electron in a strongly metal–metal bonded dimer [*cf.* 1.72 B.M. for $Re_2Cl_5(DTH)_2$][16] or a structure in which there are equal numbers of magnetically dilute rhenium(II) and rhenium(III) centers.[24]

The X-ray photoelectron spectra of these complexes (Table III) exhibit Re 4*f*, Cl 2*p*, C 1*s* and N 1*s* binding energies that are very similar. The Re 4*f* binding energies of the reduced phases are slightly lower than those of the corresponding rhenium(III) complex, consistent with, but by no means proof of, the difference in formal metal oxidation state. Both complexes possess a well resolved Cl 2*p* binding energy doublet characteristic of Re–Cl terminal bonds and there is no evidence from these ESCA spectra for the presence of Re–Cl–Re units bridging strong metal–metal bonds.[14,29,30] Of additional note is the similarity in F.W.H.M. values for the Re 4*f* binding energies of these two complexes, an indication that the reduced phase $[ReCl_{2.5}(bipy) \cdot 3/8C_4H_9OH]_n$ does not contain rhenium centers in drastically different environments as does the complex $Re_2Cl_5(DTH)_2$,[16] whose Re 4*f* binding energies are significantly broader than those of the related rhenium(III) complex $[ReCl_3(DTH)]_2$.[26]

The reactivity patterns we have observed for $]ReCl_3(DTH)]_2$ clearly show that it must possess a structure closely related to that of $[ReCl_3(PEt_3)]_2$.[17] We were therefore interested to note that Oldham and Ketteringham[27] have recently concluded, on the basis of low frequency infrared spectral studies, that it most likely possesses a structure in which the DTH ligands are chelating (structure III). However, if this were the case, the presence of the axially coordinated sulfur atoms would have a fairly pronounced effect upon the electronic absorption spectrum of this complex[31,32] and no longer would it be so closely related to that of other complexes of the type $[ReCl_3L]_2$. Accordingly, the most likely situation is for the DTH ligands to be monodentate. An alternative solid-state structure such as ionic $[Re_2Cl_4(DTH)_2]^{2+}2Cl^-$ is not supported by the ESCA spectrum of this complex[26] which shows the presence of only one type of chlorine environment.



III

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