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Complex Halides of the Transition Metals. XVIII.[1] Reduction of the Octahalodirhenate(III) Anions by Tertiary Phosphines. A New Class of Metal–Metal Bonded Dimers[2]

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Rhenium(III) chloride and the octahalodirhenate(III) anions $Re_2X_8^{2-}$, where X = Cl or Br, react with alkyl and mixed alkyl–phenyl phosphines to afford reduced phases of stoichiometry $Re_2X_5(PR_3)_3$ or $Re_2X_4(PR_3)_4$. The extent of reduction is dependent upon the degree of phenyl substitution of the phosphine. Methyldiphenyl- and ethyldiphenylphosphine produce $Re_2X_5(PRPh_2)_3$ exclusively, whereas the other phosphines all lead to a two-electron reduction. No reduction was observed when the corresponding reactions were carried out with triphenylphosphine. These phosphine complexes are derivatives of the $Re_2X_8^{3-}$ and $Re_2X_8^{4-}$ anions, neither of which has yet been stabilized in the solid state. The magnetic and spectral properties of this new class of metal–metal bonded dimers are in accord with those expected for species derived by the one- or two-electron reduction of the $Re_2X_8^{2-}$ anions. Several interesting redox reactions of these new species have been discovered including their oxidation to the $Re_2X_8^{2-}$ anions by carbon tetrachloride. For example, $Re_2Br_4(PEt_3)_4$ is oxidized in this fashion to yield a mixture of $[Et_3PCl]_2Re_2Cl_4Br_4$ and $Re_2Cl_4Br_2(PEt_3)_2$.

Introduction

In nonaqueous media, ligand molecules such as phosphines and amines will in certain circumstances induce reduction of high oxidation state transition metal halides to afford complexes of lower oxidation states.[3] The reduction of rhodium(III) chloride by triphenylphosphine to produce $RhCl(PPh_3)_3$[4] and that of molybdenum(V) chloride by alkylnitriles to yield $MoCl_4(RCN)_2$[5] are representative of this type of behavior. We recently found that the reaction of rhenium(III) chloride (Re_3Cl_9) with heterocyclic tertiary amines (e.g., pyridine and benzimidazole) results in the formation of a new class of polymeric rhenium(II) derivatives of the type $[Re_3Cl_6L_3]_n$, in which the $[Re_3Cl_3]$ cluster core of the parent halide is retained.[6] This latter reduction is particularly interesting in that it not only affords a new structural class of rhenium(II) species but it supports the belief[7] that metal halides possessing cluster structures should exhibit an extensive redox chemistry.[3] The reduction of rhenium(III) chloride by heterocyclic tertiary amines is the first instance where a *ligand-induced reduction* of this cluster halide has been observed.

We have now studied the redox behavior of the metal–metal bonded octahalodirhenate(III) anions $Re_2X_8^{2-}$ toward tertiary phosphines and have isolated a new class of rhenium(II) complexes in which a strong metal–metal bonded dimeric structure is preserved. These results are now reported in detail, together with related data on the reactions of rhenium(III) chloride with these same phosphines.[8]

Experimental Section

Rhenium(III) chloride was prepared by the thermal decomposition of commercially available rhenium(V) chloride. The salts $[(n\text{-}Bu_4N)]_2Re_2X_8$, where X = Cl or Br, and the pyridine complex $[Re_3Cl_6(py)_3]_n$ were prepared by literature methods.[6,9] All the tertiary phosphines and solvents were obtained from commercial sources. The grade of ethanol used was 200 proof. Solvents were normally deoxygenated by purging with N_2 gas for several hours.

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

A. Reactions of Rhenium(III) Chloride (Re_3Cl_9) with Tertiary Phosphines. (i) Triethylphosphine. Rhenium(III) chloride (0.15 g) was dissolved in 10 ml of dry acetone; the red solution was refluxed for a few minutes and then filtered to remove undissolved Re_3Cl_9. Triethylphosphine (0.4 ml) was added to the filtrate and the reaction mixture was refluxed for 7 days by which time it had turned dark green or brown and glistening black crystals had formed on the boiling stick. The black crystals (gray on grinding) were removed from the reaction mixture, washed well with acetone and diethyl ether, and dried in vacuo. The product analyzed for a complex of stoichiometry $[ReCl_2(PEt_3)_2]_n$. A molecular weight determination in chloroform indicated a dimeric formulation: calcd for $[ReCl_2(PEt_3)_2]_2$, 986; found, 991.

The complex was soluble in benzene, carbon tetrachloride, chloroform, dichloromethane, pyridine, and acetonitrile; it was insoluble in ethanol, methanol, diethyl ether, cyclohexane, and water. Exposure of the complex to oxygen for prolonged periods resulted in decomposition to an unidentified black oily material.

(ii) Tri-*n*-propylphosphine and Diethylphenylphosphine. The reactions of these phosphines with Re_3Cl_9 were performed as described in section A(i), using 15 ml of ethanol as the solvent. In the case of the reaction with diethylphenylphosphine, the maroon complex $Re_3Cl_9(PEt_2Ph)_3$ initially precipitated but redissolved upon prolonged reflux. After 7 days' reflux the brown reaction solution was cooled to ~10° to yield olive green $Re_2Cl_4(PEt_2Ph)_4$. The product was washed with 10 ml of ethanol and three 10-ml portions of *n*-hexane.

(iii) Ethyldiphenylphosphine and Methyldiphenylphosphine. In these reactions, Re_3Cl_9 (0.1 g) was dissolved in 30 ml of ethanol, and 1 ml of the phosphine ligand was added to this solution. The addition of ethyldiphenylphosphine resulted in the immediate precipitation of maroon $Re_3Cl_9(PEtPh_2)_3$ which gradually disappeared with formation of a light green precipitate after 2.5 days' reflux. The light green solid was filtered off and washed with diethyl ether and petroleum ether. All spectral and solubility measurements indicated the complex was identical with the product formed in the reaction of $Re_2Cl_8^{2-}$ with $PEtPh_2$ [see section B(iv)(a)]. However, the infrared and ESCA spectra of this sample showed that it was contaminated with perrhenate. This was further reflected by the microanalytical data.

In the reaction with methyldiphenylphosphine, the maroon adduct $Re_3Cl_9(PMePh_2)_3$ initially formed but it slowly disappeared with the formation of a light green precipitate after 2 days' reflux. The light green solid was filtered off, washed with diethyl ether and petroleum ether, and dried in vacuo. The product was identical with the complex formed in the reaction between $Re_2Cl_8^{2-}$ and $PMePh_2$ [see section B(iv)(a)].

(iv) Reaction of $[Re_3Cl_6(py)_3]_n$ with Triethylphosphine. Triethylphosphine (1 ml) was added to a suspension of $[Re_3Cl_6(py)_3]_n$ (0.18 g) in 10 ml of acetone. After 10 days' reflux, the solution had turned from green to brown and black crystals of $Re_2Cl_4(PEt_3)_4$ had deposited on the boiling stick. The complex was filtered off, washed with acetone and diethyl ether, and dried in vacuo.

B. Reactions of the Octahalodirhenate(III) Ions $Re_2X_8^{2-}$ with Tertiary Phosphines. (i) Trimethylphosphine. $(Bu_4N)_2Re_2Cl_8$ (0.20 g) was added to a mixture of *n*-propyl alcohol (10 ml) and trimethylphosphine (1.0 ml). The reaction mixture was refluxed for 10 days by which time the greenish brown reaction solution had yielded a crop of dark crystals (blue on grinding). These were filtered off, washed with *n*-propyl alcohol and diethyl ether, and dried in vacuo.

(ii) Triethylphosphine. A procedure similar to that described in section B(i), but using acetone (10 ml) as solvent and a 3-day reflux period, afforded black crystals of the complex $Re_2Cl_4(PEt_3)_4$. The related bromide $Re_2Br_4(PEt_3)_4$ was prepared in an identical fashion starting from $(Bu_4N)_2Re_2Br_8$. The products were filtered off, washed with acetone and diethyl ether, and dried in vacuo.

The same products were obtained when methanol (10 ml), which contained several drops of the appropriate acid HX, was used as the reaction solvent. All spectral and solubility measurements indicated the complex was identical with the product formed from the reaction of Re_3Cl_9 with PEt_3 [see section A(i)].

(iii) Tri-*n*-propylphosphine and Diethylphenylphosphine. The complexes $Re_2Cl_4(PPr_3)_4$ and $Re_2Cl_4(PEt_2Ph)_4$ were prepared from ethanol using procedure B(i). The former complex was soluble in pentane, petroleum ether, and benzene, slightly soluble in diethyl ether and acetone, and insoluble in dichloromethane, while the diethylphenylphosphine analog dissolved in dichloromethane and was slightly soluble in acetone and diethyl ether.

(iv) Ethyldiphenylphosphine and Methyldiphenylphosphine. (a) $(Bu_4N)_2Re_2Cl_8$ (0.25 g) was added to 10 ml of ethanol and then mixed with ~0.8 ml of the appropriate phosphine ligand. The reaction mixture was refluxed for 2–5 days during which time a light green insoluble material formed. The complex was filtered off, washed with several portions of ethanol, diethyl ether, and petroleum ether, and dried in vacuo. Both complexes analyzed for the stoichiometry $[ReCl_{2.5}(PRPh_2)_{1.5}]_n$.

The product from the ethyldiphenylphosphine reaction was purified by recrystallization from benzene. The same product was obtained if the reaction was performed in *n*-butyl alcohol or if acetone was used (10 days' reflux). In the latter solvent the product was forced out of solution by the addition of ethanol. A molecular weight measurement on a solution of this complex in 1,2-dichloroethane, a solvent from which it could be recovered unchanged, showed that the complex possessed a dimeric formulation: calcd for $Re_2Cl_5[P(C_2H_5)(C_6H_5)_2]_3$, 1191; found, 1099.

Solubility measurements on the analogous light green methyldiphenylphosphine product showed that it was insoluble in acetone, methanol, benzene, dichloromethane, tetrahydrofuran, and acetonitrile.

(b) $(Bu_4N)_2Re_2Br_8$ (0.2 g) was dissolved in 10 ml of methanol containing 5 drops of 48% HBr (to suppress solvolysis), and 0.5 ml of the phosphine was added to the resulting green solution. A red-brown precipitate initially formed (the adduct $Re_2Br_6(PRPh_2)_2$), but this redissolved on heating, and during a further 48 hr of reflux, the appropriate yellow-green complex $Re_2Br_5(PRPh_2)_3$ precipitated. The insoluble product was filtered off, washed with small portions of methanol and diethyl ether, and dried in vacuo.

C. Reactions of the Reduced Rhenium Halide–Phosphine Complexes. (i) Reaction of $Re_2Cl_4(PEt_3)_4$ with Methanol–HCl. A small quantity of $Re_2Cl_4(PEt_3)_4$ (0.25 g) was added to methanol (10 ml) to which 6 drops of concentrated hydrochloric acid had been added. The reaction mixture was refluxed for 3 days during which time the complex slowly dissolved to give a green solution. This solution was then evaporated, using a rotary evaporator, until precipitation of a green solid commenced, and it was then refrigerated overnight. The green solid was filtered off, washed with diethyl ether and petroleum ether, and dried in vacuo. The microanalysis of the green product agreed with the formulation $Re_2Cl_6(PEt_3)_2$. Anal. Calcd for $Re_2Cl_6[P(C_2H_5)_3]_2$: C, 17.5; H, 3.7. Found (for separate preparative samples): C, 17.4, 17.5; H, 3.7, 3.7; yield ~70%. The green complex could be recrystallized from benzene solution, but the recovered complex contained *variable* amounts of solvated benzene. Anal. Calcd for $Re_2Cl_6[P(C_2H_5)_3]_2\cdot{}^1/_6C_6H_6$: C, 18.7; H, 3.7; Cl, 25.5. Found: C, 18.6; H, 4.0; Cl, 25.5. Calcd for $Re_2Cl_6[P(C_2H_5)_3]_2\cdot{}^1/_2C_6H_6$: C, 20.9; H, 3.8; Cl, 24.8. Found: C, 21.3; H, 3.8; Cl, 24.7. When the recrystallized material was washed with diethyl ether and/or dried in vacuo, the crystals reverted back to a powder due to loss of benzene.

(ii) Reactions with Carbon Tetrachloride. (a) $Re_2Cl_4(PEt_3)_4$. A sample of $Re_2Cl_4(PEt_3)_4$ (0.1 g) was dissolved in 10 ml of carbon tetrachloride to produce a clear green solution. After the solution had been refluxed for 1 day, a sticky blue solid precipitated. The carbon tetrachloride supernatant was decanted off, and the remaining solid was stirred with 25 ml of acetone for 30 min, filtered off, and finally washed with separate portions of ethanol, benzene, and diethyl ether. Its microanalytical data were in accord with those expected for $(Et_3PCl)_2Re_2Cl_8$. Anal. Calcd for $[(C_2H_5)_3PCl]_2Re_2Cl_8$: C, 14.9; H, 3.1; Cl, 36.9. Found: C, 14.7; H, 3.4; Cl, 37.2; yield ~85%. In addition, a cation-exchange reaction was carried out by dissolving a sample of $(Et_3PCl)_2Re_2Cl_8$ (0.15 g) in methanol (containing several drops of concentrated hydrochloric acid) and then adding 0.3 g of tetraphenylarsonium chloride. This caused the precipitation of the well-characterized blue complex $(Ph_4As)_2Re_2Cl_8$.[10] This complex was washed with methanol and diethyl ether. Anal. Calcd for $[(C_6H_5)_4As]_2Re_2Cl_8$: C, 40.5; H, 2.8. Found: C, 40.5; H, 2.9; yield ~75%.

(b) $Re_2Br_4(PEt_3)_4$. A green solution containing 0.15 g of $Re_2Br_4(PEt_3)_4$ dissolved in 10 ml of carbon tetrachloride was refluxed for 0.5 hr to produce a green oil which deposited on the walls of the flask. The now colorless carbon tetrachloride solution was decanted off, and acetone (25 ml) was added to the flask. When the acetone and green oil mixture was stirred at room temperature for 1 hr, the oil transformed to a light green powder which was filtered off leaving an emerald green acetone solution. The yield of this light green powder was increased by refluxing and stirring the mixture for 24 hr instead of maintaining it at room temperature for 1 hr. The complex was washed with acetone, diethyl ether, and petroleum ether and dried in vacuo. This product analyzed closely for $Re_2Cl_4Br_2(PEt_3)_2\cdot{}^1/_3CCl_4$. Anal. Calcd for $Re_2Cl_4Br_2[P(C_2H_5)_3]\cdot{}^1/_3CCl_4$: C, 15.4; H, 3.1; Cl, 19.7; Br, 16.6. Found (for separate preparative samples): C, 15.4, 15.6; H, 3.1, 3.3; Cl, 20.1, 20.0; Br, 17.1, 17.2. The remaining emerald green acetone solution was then evaporated using a rotary evaporator until green crystals began to form, and the solution was then refrigerated overnight. The green crystals were filtered off, washed with the filtrate, followed by 2 ml of acetone and diethyl ether, and dried in vacuo. The yield of this product was drastically reduced if the original green oil–acetone mixture was refluxed instead of stirred at room temperature. The microanalytical data for this product showed that it was the salt $(Et_3PCl)_2Re_2Cl_4Br_4$. Anal. Calcd for $[(C_2H_5)_3PCl]_2Re_2Cl_4Br_4$: C, 12.6; H, 2.6; Cl, 18.7; Br, 28.0. Found: C, 13.0; H, 2.7; Cl, 19.0; Br, 28.3.

$(Et_3PCl)_2Re_2Cl_4Br_4$ (0.1 g) was dissolved in 10 ml of acetone, and to this was added 0.1 g of triphenylphosphine. The reaction mixture was heated for 30 min and then evaporated to a volume of 2–3 ml. Methanol was then added to this solution to precipitate a tan solid that was filtered off, washed with methanol and diethyl ether, and dried in vacuo. The complex analyzed as the adduct $Re_2Cl_4Br_2(PPh_3)_2$. Anal. Calcd for $Re_2Cl_4Br_2[P(C_6H_5)_3]_2$: C, 36.1; H, 2.5; Cl, 11.9; Br, 13.3. Found: C, 36.4; H, 2.9; Cl, 12.1; Br, 13.0; yield ~70%.

(c) $Re_2Cl_5(PEtPh_2)_3$ and $Re_2Cl_4(PEt_2Ph)_4$. A mixture of tetraphenylarsonium chloride (0.8 g) and $Re_2Cl_5(PEtPh_2)_3$ (0.1 g) was dissolved in a mixture of carbon tetrachloride (5 ml) and dichloromethane (5 ml). The solution was then refluxed for 20 hr whereupon the blue crystalline product $(Ph_4As)_2Re_2Cl_8$ precipitated; yield ~92%. The infrared spectrum of the complex (4000–200 cm^{-1}) confirmed its identity. An exactly analogous reaction occurred with the complex $Re_2Cl_4(PEt_2Ph)_4$ to produce $(Ph_4As)_2Re_2Cl_8$.

(iii) Reaction of $Re_2Cl_5(PEtPh_2)_3$ with Triethylphosphine. $Re_2Cl_5(PEtPh_2)_3$ (0.15 g) was dissolved in 9 ml of acetone, 1 ml of triethylphosphine was added, and the reaction mixture was refluxed for 2 days. By this time, crystals of $Re_2Cl_4(PEt_3)_4$ had formed on the boiling stick, and they were filtered off, washed with acetone and diethyl ether, and dried in vacuo; yield ~50%. The infrared and electronic spectra of this complex confirmed its identity.

D. Preparation of the Dinuclear Rhenium(III) Phosphine Complexes. The complexes $Re_2Cl_6(PR_3)_2$, where PR_3 represents PEt_3, $P(n\text{-}Pr)_3$, $PEtPh_2$, $PMePh_2$, PPh_3, and PEt_2Ph, and the bromo complex $Re_2Br_6(PEtPh_2)_2$ were generally prepared according to procedures described in the literature[9,11,12] using methanol–HX as the reaction solvent. The complexes with $PMePh_2$, $PEtPh_2$, and PEt_2Ph have not previously been reported before. In the synthesis of the triethylphosphine complex, it was noted that even with very mild heating of the reaction solution, reduction to $Re_2Cl_4(PEt_3)_4$ began to occur. Accordingly, it was necessary in this preparation to cool the stirred reaction mixture with ice to prevent reduction from occurring. For the isolation of $Re_2Cl_6(PEt_2Ph)_2$, the reaction solvent used was changed to a mixture of 15 ml of *n*-propyl alcohol, 10 ml of methanol, and 1 ml of concentrated hydrochloric acid. In this case the phosphine complex precipitated after refrigerating the mixture for 12 hr. Representative microanalytical data follow. Anal. Calcd for $Re_2Cl_6[P(C_2H_5)(C_6H_5)_2]_2$: C, 33.2; H, 3.1. Found: C, 33.1; H, 3.1; yield ~85%.

Physical Measurements. Infrared spectra in the region 4000–200 cm^{-1} were recorded as Nujol mulls using a Beckman IR-12 spectrophotometer. Raman spectra were obtained on the Purdue Mark II laser Raman spectrometer using 5145-Å excitation. Electronic spectra were recorded on a Cary 14 spectrophotometer. Magnetic moments were measured by the Gouy method using $Hg[Co(SCN)_4]$ as the calibrant. Corrections for the ligand diamagnetism were

Table I. Products of the Reactions of the Octahalodirhenate(III) Anions and Rhenium(III) Chloride with Tertiary Phosphines

No.	Complex	Starting material	% C Calcd	% C Found	% H Calcd	% H Found	% halogen Calcd	% halogen Found	% yield
I	$Re_2Cl_4[(P(CH_3)_3]_4$	$[(C_4H_9)_4N]_2Re_2Cl_8$	17.6	17.6	4.4	4.6			60
II	$Re_2Cl_4[P(C_2H_5)_3]_4$	$[(C_4H_9)_4N]_2Re_2Cl_8$	29.2	29.0	6.1	6.2	14.4	14.7	72
		Re_3Cl_9	29.2	29.3	6.1	6.2	14.4	14.6	50
		$[Re_3Cl_6(py)_3]_n$	29.2	29.3	6.1	6.1			35
III	$Re_2Br_4[P(C_2H_5)_3]_4$	$[(C_4H_9)_4N]_2Re_2Br_8$	24.7	24.7	5.2	5.0			60
IV	$Re_2Cl_4[P(C_3H_7)_3]_4$	$[(C_4H_9)_4N]_2Re_2Cl_8$	37.4	37.1	7.3	7.1			60
		Re_3Cl_9	37.4	37.2	7.3	7.4			40
V	$Re_2Cl_4[P(C_2H_5)_2(C_6H_5)]_4$	$[(C_4H_9)_4N]_2Re_2Cl_8$	40.7	39.5	5.1	5.1	12.1	12.1	50
		Re_3Cl_9	40.7	39.6	5.1	5.2			28
VI	$Re_2Cl_5[P(CH_3)(C_6H_5)_2]_3$	$[(C_4H_9)_4N]_2Re_2Cl_8$	40.7	40.7	3.4	3.3	15.4	15.4	90
		Re_3Cl_9	40.7	40.6	3.4	3.5	15.4	15.5	50
VII	$Re_2Cl_5[P(C_2H_5)(C_6H_5)_2]_3$	$[(C_4H_9)_4N]_2Re_2Cl_8$	42.3	42.5	3.8	3.9	14.9	14.7	75
		Re_3Cl_9	42.3	40.8	3.8	4.0	14.9	14.0	45
VIII	$Re_2Br_5[P(C_2H_5)(C_6H_5)_2]_3$	$[(C_4H_9)_4N]_2Re_2Br_8$	35.6	35.8	3.2	3.3	28.3	28.1	60
IX	$Re_2Br_5[P(CH_3)(C_6H_5)_2]_3$	$[(C_4H_9)_4N]_2Re_2Br_8$	34.1	34.3	2.8	2.9	29.1	29.3	60

estimated from Pascal's constants.

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.

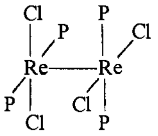
Results and Discussion

(a) Synthesis and Preliminary Characterization. In contrast to the reactions of rhenium(III) chloride with heterocyclic tertiary amines, in which the reduced phases $[Re_3Cl_6L_3]_n$ were isolated,[6] the reaction of this halide with the tertiary phosphines PEt_3, $P(n\text{-}Pr)_3$, and PEt_2Ph (Table I) affords crystalline complexes of stoichiometry $[ReCl_2(PR_3)_2]_n$ via the intermediate unreduced adducts $Re_3Cl_9(PR_3)_3$. Preliminary characterization studies were carried out on the triethylphosphine complex $[ReCl_2(PEt_3)_2]_n$. A molecular weight measurement in chloroform showed that the complex was dimeric and PMR measurements in this same solvent indicated that it was not a rhenium(III)–hydrido complex. This latter conclusion was further supported by the infrared spectrum (4000–600 cm^{-1}) of this complex which revealed the absence of ν(Re–H) modes. The infrared spectrum was typical of coordinated triethylphosphine and showed that the complex was free of perrhenate and hydroxide contaminants. The complex was diamagnetic at room temperature ($\chi_g = -0.494 \times 10^{-6}$ cgsu at 296°K) thereby confirming that it was not a magnetically dilute rhenium(II) species.

The dimeric nature of this complex was considered reasonable in view of the well-known disruption of Re_3Cl_9 by molten diethylammonium chloride to produce $(Et_2NH_2)_2Re_2Cl_8$.[13,14] Our observations on the phosphine reactions suggested to us that complexes of the type $Re_2Cl_4(PR_3)_4$ should be obtainable directly from the octachlorodirhenate(III) anion. Previous reports[9,11,12] clearly showed that this dianion and its bromo analog react with tertiary phosphines to form the dimers $Re_2X_6(PR_3)_2$, but there was no documented evidence to suggest that reduction was very likely. However, we found that the reaction of the salt $(Bu_4N)_2Re_2Cl_8$ with PMe_3, PEt_3, $P(n\text{-}Pr)_3$, and PEt_2Ph readily leads to reduction and the isolation of the dimers $Re_2Cl_4(PR_3)_4$ in good yield (Table I). These complexes had identical properties to the products of this same stoichiometry isolated from the reactions of rhenium(III) chloride with phosphines. Such behavior should also be exhibited by the related bromo anion, and indeed the reaction of $(Bu_4N)_2Re_2Br_8$ with PEt_3 gave $Re_2Br_4(PEt_3)_4$ in 60% yield.

Both the disruption of the Re_3Cl_9 cluster and the extent of reduction were critically dependent upon the degree of phenyl substitution of the phosphine. With $PMePh_2$ and $PEtPh_2$ both Re_3Cl_9 and $(Bu_4N)_2Re_2Cl_8$ reacted to produce complexes of stoichiometry $[ReCl_{2.5}(PR_3)_{1.5}]_n$. A molecular weight measurement on a 1,2-dichloroethane solution of the $PEtPh_2$ complex showed it to be dimeric $Re_2Cl_5(PEtPh_2)_3$, which is formally derived from diamagnetic $Re_2Cl_6(PEtPh_2)_2$ by a one-electron reduction. This was further confirmed by a magnetic susceptibility measurement which showed this complex to be paramagnetic (μ_{eff} = 2.0 BM) at room temperature. As expected, the reaction of $(Bu_4N)_2Re_2Br_8$ with $PMePh_2$ and $PEtPh_2$ proceeded in an identical fashion to yield $Re_2Br_5(PR_3)_3$ (Table I). Triphenylphosphine reacted with Re_3Cl_9 and $(Bu_4N)_2Re_2Cl_8$ to afford the already well-characterized species $Re_3Cl_9(PPh_3)_3$[15] and $Re_2Cl_6(PPh_3)_2$.[9] Irrespective of the reaction conditions we used, neither disruption of the Re_3Cl_9 cluster nor reduction of $Re_2Cl_6(PPh_3)_2$ occurred. Therefore, the tendency for phosphine-induced reduction decreases with increasing phenyl substitution.

(b) Molecular Structure of $Re_2Cl_4(PEt_3)_4$. Suitable single crystals of this complex were obtained for an X-ray structure analysis, preliminary details of which have been reported.[8a] The $Re_2Cl_4P_4$ skeleton has the eclipsed noncentrosymmetric D_{2d} structure I, in which the Re–Re distance (2.23 Å) is the same as that in $Re_2Cl_6(PEt_3)_2$[11] and other quadruply bonded dirhenium(III) complexes.[16] The individual $ReCl_2P_2$ units are nonplanar due to strong repulsion effects between the halves of the molecule. Increasing substitution of *n*-alkyl substituents on the phosphine by phenyl groups should lead to a further increase in these intramolecular repulsions and eventually to instability of the dimer. This is borne out within the series PEt_3, PEt_2Ph, $PEtPh_2$, and PPh_3, for which the final products are $Re_2Cl_4(PEt_3)_4$, $Re_2Cl_4(PEt_2Ph)_4$, $Re_2Cl_5(PEtPh_2)_3$, and $Re_2Cl_6(PPh_3)_2$, respectively. This is a clear indication that steric effects control the degree to which reduction can occur. The constancy of the number of ligand groups attached to the two rhenium atoms suggests a close structural relationship between $Re_2X_4(PR_3)_4$ and $Re_2X_5(PR_3)_3$ (see Results and Discussion, sections c and d).



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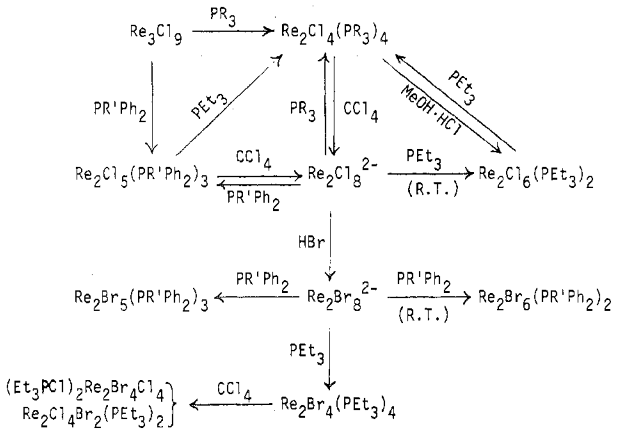
The close structural relationship between $Re_2X_4(PR_3)_4$, $Re_2X_5(PR_3)_3$, and $Re_2X_6(PR_3)_2$ suggested to us that a variety of interesting chemical reactions should be exhibited by the reduced phases to afford reaction products in which the strongly metal–metal bonded unit would very likely be preserved. In particular, we suspected that the interconversion between these three oxidation states would be particularly facile and that such reactivity patterns would be useful in establishing the presence or absence of the Re_2 unit in phases of unknown structure.

(c) Reactions of Complexes of the Types $Re_2X_4(PR_3)_4$ and $Re_2X_5(PR_3)_3$. The reactions of these complexes are in accord

Scheme I. Reactions of Tertiary Phosphine Complexes of Rhenium[a]



[a] PR_3 = PMe_3, PEt_3, $P(n\text{-}Pr)_3$, or PEt_2Ph, and R' = Me or Et for $PR'Ph_2$; RT signifies that the reaction was carried out at room-temperature.

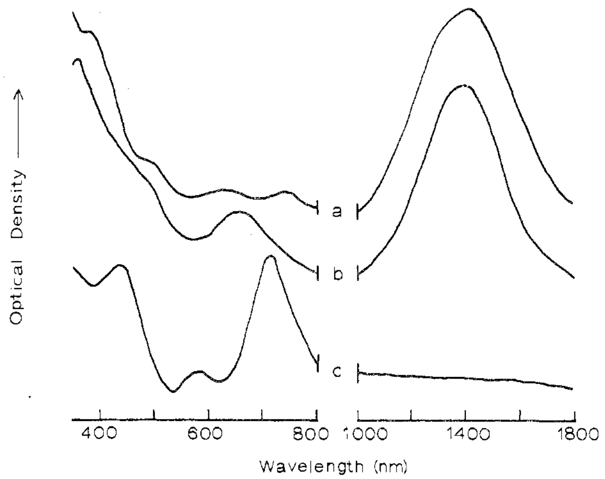


Figure 1. Electronic absorption spectra (Nujol mulls) of (a) $Re_2Cl_5(PEtPh_2)_3$, (b) $Re_2Cl_4(PEt_3)_4$, and (c) $Re_2Cl_6(PEtPh_2)_2$.

with their dinuclear structures (see Scheme I). From an earlier study[6] we had shown that the reaction of heterocyclic amine complexes of the type $[Re_3Cl_6L_3]_n$ with methanolic HCl afforded the rhenium(III) salts $[LH]_2Re_3Cl_{11}$, an observation which strongly suggested that the trinuclear Re_3 cluster of the parent halide Re_3Cl_9 was retained in the reduced phases. The related reaction of $Re_2Cl_4(PEt_3)_4$ with methanolic HCl produced the well-characterized[11] rhenium(III) complex $Re_2Cl_6(PEt_3)_2$. Oxidation to a rhenium(III) species was also achieved upon refluxing $Re_2Cl_4(PEt_3)_4$ with carbon tetrachloride. In this case, the blue complex $(Et_3PCl)_2Re_2Cl_8$ was isolated and this in turn was readily converted to $(Ph_4As)_2Re_2Cl_8$ via a cation-exchange reaction. In addition to the infrared and electronic absorption spectra of $(Et_3PCl)_2Re_2Cl_8$ which readily confirmed its identity, the X-ray photoelectron spectrum of this complex exhibited two sets of chlorine 2p core binding energies (separated by ~1.6 eV). These were in the intensity ratio 1:4 and could be readily assigned to cationic and anionic chlorine environments.[17] When other complexes of the type $Re_2Cl_4(PR_3)_4$ reacted with refluxing carbon tetrachloride, pure products could not be isolated. We suspect that this is merely a reflection of the inability of the other tertiary phosphines to form stable cationic species of the type $(R_3PCl)^+$. A result which supports this contention is our observation that when the complex $Re_2Cl_4(PEt_2Ph)_4$ was allowed to react with a mixed dichloromethane–carbon tetrachloride solvent system to which tetraphenylarsonium chloride had been added, $(Ph_4As)_2Re_2Cl_8$ was produced in high yield. This shows that the $Re_2Cl_8{}^{2-}$ anion is generated irrespective of the nature of the phosphine.

The related reactivity patterns of $Re_2Cl_5(PEtPh_2)_3$ strongly support the presence of a strong Re–Re bond. Reaction with an excess of triethylphosphine produced $Re_2Cl_4(PEt_3)_4$, while treatment with a mixed dichloromethane–carbon tetrachloride solvent containing tetraphenylarsonium chloride gave the oxidation product $(Ph_4As)_2Re_2Cl_8$. The oxidation of $Re_2Cl_4(PEt_3)_4$ by carbon tetrachloride led us to suspect that the related oxidation of $Re_2Br_4(PEt_3)_4$ might afford a novel mixed-halide complex with the $Re_2X_8{}^{2-}$ structure. Mixed halides of the type $Re_2Cl_{8-n}Br_n{}^{2-}$ were recently reported to be formed by the reaction of the $Re_2Cl_8{}^{2-}$ anion with hydrobromic acid.[19] However, this particular technique can easily lead to a mixture of such phases whose composition averages out to the observed stoichiometry. We felt that the carbon tetrachloride oxidation would provide a feasible route to a homogeneous mixed-halide complex. The reaction of $Re_2Br_4(PEt_3)_4$ with carbon tetrachloride resulted in the formation of a green oil which when treated with acetone yielded a pale green insoluble product, $Re_2Cl_4Br_2(PEt_3)_2$, and from the green acetone filtrate crystals of the salt $[Et_3PCl]_2Re_2Cl_4Br_4$ could be isolated. Interestingly, the yield of the salt was greatest when the acetone–oil mixture was stirred but not refluxed; refluxing and stirring of this mixture for a long period resulted in almost complete conversion to the adduct $Re_2Cl_4Br_2(PEt_3)_2$. Since 4 mol of phosphine ligand are released during the oxidation to $(Et_3PCl)_2Re_2Cl_4Br_4$ and only 2 mol of phosphine are required to form the counterion, it seemed likely that once the $Re_2Cl_4Br_4{}^{2-}$ anion had been generated it would then react with the excess phosphine in the system to afford the adduct $Re_2Cl_4Br_2(PEt_3)_2$. To substantiate this interpretation, the salt $(Et_3PCl)_2Re_2Cl_4Br_4$ was allowed to react with PPh_3, and the expected formation of $Re_2Cl_4Br_2(PPh_3)_2$ was observed.

(d) Electronic and Low-Frequency Vibrational Spectra. It is not our purpose at the present time to propose detailed assignments of the electronic absorption spectra of the complexes but rather to report structure-related correlations. It is apparent from examination of the electronic absorption spectral data summarized in Table II and illustrated in Figure 1 that we can make several important diagnostic observations. The spectra of the rhenium(III) complexes of the types $Re_2X_8{}^{2-}$ and $Re_2X_6(PR_3)_2$ (Table II), in which a strong Re–Re bond is known to exist, show their lowest energy electronic transition between 695 and 760 nm, together with several additional (usually less intense) features between 580 and 340 nm. These spectra are very similar to those reported in the literature for related species.[10,12,20] The low-energy transition has recently been attributed to the $\delta(b_{2g}) \rightarrow \delta^*(b_{1u})$ excitation[21] on the basis of detailed single-crystal spectral studies on $(Bu_4N)_2Re_2Cl_8$ and $Re_2Cl_6(PEt_3)_2$.[22] On the other hand, the complexes $Re_2X_5(PR_3)_3$ exhibit a very intense absorption in the near-infrared region at ~1400 nm (Figure 1 and Table II). A similar feature was sometimes observed in both the solution and solid-state spectra of the two-electron reduced species $Re_2X_4(PR_3)_4$, but there is good evidence that in these instances it is due to the presence of a species which arises from oxidation of $Re_2X_4(PR_3)_4$.[23] Dry, oxygen-free benzene, dichloromethane or pentane solutions of $Re_2Cl_4(PR_3)_4$ do not show an absorption band in this region. However, when these solutions are exposed to the atmosphere, an extremely intense band grows in at ~1380 nm. This change is not accompanied by a very dramatic modification in any of the other spectral features provided the solutions are exposed to the atmosphere for less than ~30 min. While oxidation is very rapid in solution when solvents, *particularly dichloromethane*, are not rigorously dried and deoxygenated,

Table II. Spectral Properties of Dinuclear Rhenium Complexes

Complex	Medium	Electronic absorption Maxima, nm[a]	Infrared spectra, ν(Re-X), cm^{-1}
$Re_2Cl_4(PEt_3)_4$	NM[d]	1384 s,[b] 650 m, 492 sh, 365 s	325 s, 305 m
	Benzene	763 sh, 652 (140), 540 sh, 510 (100), 420 (95), 364 sh	
$Re_2Cl_4[P(n\text{-}Pr)_3]_4$	NM	1325 m,[b] 770 sh, 640 m, 540 sh, 494 m, 365 s	318 s, 295 m
	Pentane	760 sh, 645 (138), 542 sh, 498 (100), 415 (85), 361 sh	
$Re_2Cl_4(PEt_2Ph)_4$	NM	770 sh, 645 m, 520 m, 425 sh, 375 sh	324 s, 303 m
	CH_2Cl_2	765 (75), 635 (187), 505 sh, 420 sh	
$Re_2Br_4(PEt_3)_4$	NM	1382 s,[b] 650 m, 550 sh, 500 sh, 440 sh, 405 s	*c*
$Re_2Cl_5(PEtPh_2)_3$	NM	1400 s, 740 w, 630 w, 488 sh, 420 sh, 381 sh	342 s, 317 m, 304 sh
	CH_2Cl_2	1375 (2700), 755 (50), 638 (120), 485 sh, 420 sh, 388 (1600), 343 sh	
$Re_2Cl_5(PMePh_2)_3$	CH_2Cl_2	1350 s, 730 vw, 630 vw, 473 sh, 378 m	342 s, 318 m–s, 309 sh
$Re_2Br_5(PEtPh_2)_3$	NM	1430 s, 750 vw, 525 sh, 430 m	250 m, 222 m
$Re_2Br_5(PMePh_2)_3$	NM	1475 s, 750 vw, 524 sh, 438 m	246 m, 221 m
$Re_2Cl_6(PEt_3)_2$	NM	720 s, 575 sh, 450 sh, 375 m–s	350 vs, 304 s
$Re_2Cl_6[P(n\text{-}Pr)_3]_2$	NM	720 s, 575 w, 455 sh, 390 m–s	350 vs, 310 s
$Re_2Cl_6(PEt_2Ph)_2$	NM	720 s, 575 w, 450 m, 350 sh	348 vs, 310 s
$Re_2Cl_6(PEtPh_2)_2$	NM	715 s, 580 w, 440 m, 340 sh	353 vs, 311 s
$Re_2Cl_6(PMePh_2)_2$	CH_2Cl_2	720 s, 570 vw, 410 m, 370 sh	355 vs, 315 s
$Re_2Br_6(PEtPh_2)_2$	NM	760 s, 450 s	250 sh, 236 s
$Re_2Cl_4Br_2(PEt_3)_2$	NM	700 s, 580 sh, 420 sh	338 vs, 314 sh, 241 s, 224 sh
$[Et_3PCl]_2Re_2Cl_4Br_4$	Acetone	695 m, 420 sh	338 vs, 313 sh, 240 s, 218 sh
$[Et_3PCl]_2Re_2Cl_8$	NM	693 s, 572 vw, 463 sh, 361 m	337 s

[a] Molar extinction coefficients are given in parentheses. [b] These absorption bands arise from the presence of small amounts of oxidation product (see Results and Discussion section). [c] No bands above 210 cm^{-1} assignable to ν(Re–Br). [d] Nujol mull.

it also usually occurs upon grinding the solids, as evidenced by the Nujol mull electronic spectra (Figure 1 and Table II) of all complexes of the type $Re_2X_4(PR_3)_4$, except $Re_2Cl_4(PEt_2Ph)_4$. Spectral trace (b) in Figure 1 shows the intense impurity band at 1384 nm. With the exception of this absorption, the spectrum is otherwise that of authentic $Re_2Cl_4(PEt_3)_4$. Since the paramagnetic complexes $Re_2X_5(PR_3)_3$ exhibit an intense band in this same spectral region,[25] it is likely that the oxidation of $Re_2X_4(PR_3)_4$ leads to $Re_2X_5(PR_3)_3$ or some structurally related species. This behavior is being further investigated in this laboratory.

Based on Cotton's molecular orbital description of the bonding in these dimers,[21,28] in the two-electron reduction from $Re_2X_8{}^{2-}$ (or $Re_2X_6(PR_3)_2$) to $Re_2X_4(PR_3)_4$, the ground state configuration change is from $\sigma^2\pi^4\delta^2$ to one in which a nonbonding orbital (probably that of a_{2u} symmetry) is occupied, thereby giving a $\sigma^2\pi^4\delta^2\sigma^2$ set. That it is a nonbonding orbital singlet which contains the two electrons, rather than the antibonding $\delta^*(b_{1u})$ orbital, is required by the observed diamagnetism of the complexes, the unchanged Re–Re distance, and the eclipsed configuration.

From the recent work of Norman and Kolari[24] an alternative interpretation is possible for the observed diamagnetism and molecular structure of $Re_2X_4(PR_3)_4$. Using the $X\alpha$ scattered-wave method, a first-principles MO calculation on the $Mo_2Cl_8{}^{4-}$ anion (which is isostructural with $Re_2Cl_8{}^{2-}$) indicates[24] that the two metal nonbonding a_{1g} and a_{2u} orbitals are not close in energy to the $\delta^*(b_{1u})$ orbital. However, there are two empty singlet states, of b_{1g} and b_{2u} symmetry, which are metal–ligand *antibonding orbitals* and are near in energy to the δ^* orbital, thus filling the same role as the a_{1g} and a_{2u} orbitals in Cotton's description.

The infrared spectra of all the complexes were recorded over the range 4000–200 cm^{-1}. General features in the 4000–400-cm^{-1} region verified the presence of coordinated phosphine ligands, and a survey of the 750–1000-cm^{-1} region showed the absence of bands assignable to rhenium–oxygen impurities. The low-frequency infrared data (400–200 cm^{-1}) are summarized in Table II and representative spectra are shown in Figure 2. The observed shift of the ν(Re–Cl) bands to lower energies in the sequence $Re_2Cl_6L_2 > Re_2Cl_5L_3 > Re_2Cl_4L_4$ is consistent with the decrease in metal oxidation state. The infrared data on the bromide systems parallel the results for the related chlorides.

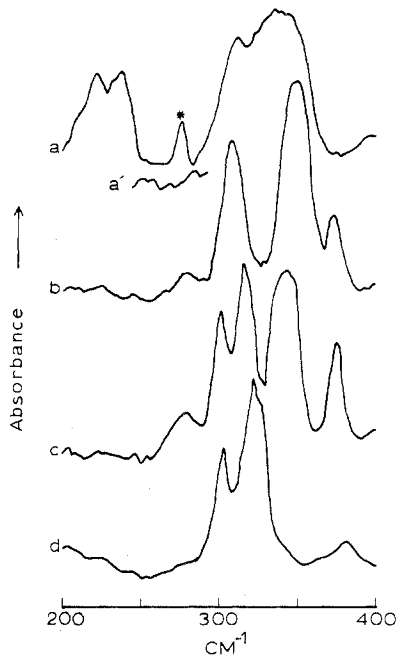
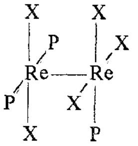


Figure 2. Low-frequency infrared spectra (Nujol mulls) of (a) $(Et_3PCl)_2Re_2Br_4Cl_4$, (b) $Re_2Cl_6(PEtPh_2)_2$, (c) $Re_2Cl_5(PEtPh_2)_3$, and (d) $Re_2Cl_4(PEt_3)_4$. The asterisk in spectrum a denotes the band assigned to ν(Re–Re); the trace a′ shows the related spectrum of $(Et_3PCl)_2Re_2Cl_8$ in this region.

The mixed-halide species $Re_2Cl_4Br_4{}^{2-}$ and $Re_2Cl_4Br_2(PEt_3)_2$ both exhibit a weak infrared-active band at 277 cm^{-1} which is probably the ν(Re–Re) mode,[29,30] now activated as a result of their possessing low-symmetry structures. Unfortunately, there are such a large number of dimeric $[Re_2X_8]$ type structures possible which could exhibit an infrared-active ν(Re–Re) band[31] that we are unable to specify exactly which isomer (or mixture of isomers) has been generated.

The Raman spectrum of a benzene solution of the complex $Re_2Cl_5(PEtPh_2)_3$ exhibited an intense polarized line at 277 cm^{-1}, which is readily assigned to the ν(Re–Re) mode by comparison with related measurements on the $Re_2Cl_8^{2-}$ anion.[29] The presence of this frequency in the Raman spectrum is entirely consistent with the retention of a quadruple Re–Re bond in this complex. In the light of this observation and the previously discussed reactivity patterns exhibited by complexes of this type and by bearing in mind the structural features of $Re_2Cl_4(PEt_3)_4$,[8a] we suggest that the phosphine complexes $ReX_5(PR_3)_3$ possess the eclipsed configuration shown in structure II.



II

(e) Some Concluding Remarks and the Relationship of the Complexes $Re_2X_4(PR_3)_4$ and $Re_2X_5(PR_3)_3$ to Dimers of Technetium and Molybdenum. The failure of phosphines to yield complexes of the type $[Re_3Cl_6(PR_3)_3]_n$, analogous to the amine complexes, can be attributed in part to differing steric requirements of these ligand molecules. Structural data available for the adduct $Re_3Cl_9(PEt_2Ph)_3$[32] reveal the rather weak nature of the Re–P bonds, a feature which arises from unfavorable nonbonded repulsions between the phosphine and chloride ligands. If reduction is to occur, a much closer approach of the phosphine is presumably required in order to facilitate the necessary charge transfer. Accordingly, we would not expect a phosphine analog of $[Re_3Cl_6(py)_3]_n$ to be stable, and the only reasonable alternative is for the Re_3Cl_9 cluster to be disrupted. The observed formation of $Re_2Cl_4(PR_3)_4$ or $Re_2Cl_5(PR_3)_3$ is in accord with this. A further observation which is of relevance to this conclusion is the failure of triethylphosphine to convert $[Re_3Cl_6(py)_3]_n$ to $[Re_3Cl_6(PEt_3)_3]_n$. Instead, this reaction affords another route to the dimer $Re_2Cl_4(PEt_3)_4$.

The complexes $Re_2Cl_4(PR_3)_4$ and $Re_2Cl_5(PR_3)_3$ are formally phosphine derivatives of the $Re_2Cl_8^{4-}$ and $Re_2Cl_8^{3-}$ anions, neither of which has yet been isolated in the solid state although there is polarographic evidence that they can be generated in acetonitrile.[33] Of the related technetium chloro anions, only salts of the $Tc_2Cl_8^{3-}$ anion have been isolated. All of the available evidence points to a close structural relationship between $Tc_2Cl_8^{3-}$ and $Re_2Cl_5(PR_3)_3$.

It has already been established that there is a striking structural relationship between the isoelectronic $Re_2Cl_8^{2-}$ and $Mo_2Cl_8^{4-}$ anions[34] and the same relationship presumably exists between $Re_2Cl_6(PR_3)_2$ and the complexes of the type $Mo_2Cl_4(PR_3)_4$ which have recently been isolated by San Filippo.[12,35] This is supported by our structural studies on $Re_2Cl_4(PEt_3)_4$ which show that it possesses an analogous structure to $Re_2Cl_6(PEt_3)_2$ in spite of the two-electron reduction.

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