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Some Reactions of the Octahalodirhenium(III) Ions.
I. Reactions with Phosphines[1]

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The reactions of the $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ ions with triphenylphosphine and with 1,2-bis(diphenylphosphino)ethane (diphos) have been studied. With $P(C_6H_5)_3$ the products isolated were $[ReX_3P(C_6H_5)_3]_n$ in which n is thought to be 2, although the insolubility of the compounds prevented obtaining direct proof. With diphos three types of compounds can be obtained depending on the solvent used, the time, and, especially, the temperature of reaction and workup. $[Re(diphos)Cl_3]_n$ appears to be an authentic ReX_3L_2-type Re(III) complex; it can be oxidized to $[Re(diphos)Cl_3O]$, and this can be converted to $[ReCl_3(diphos)NC_6H_5]$. The four compounds $[Re(diphos)_2X_2]Y$ (X = Cl or Br; Y = X or ClO_4) appear to contain six-coordinate, mononuclear Re(III) complexes, a class of which there are few examples. $[Re(diphos)_2O_2]ClO_4$ provides a new example of a *trans*-dioxo Re(V) complex. The known coordination chemistry of rhenium in its lower oxidation states, II–V, is reviewed. Modified preparative conditions giving ~40% yield of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$, a 2-fold increase, are described.

Introduction

The coordination chemistry of rhenium in its lower oxidation states, II–V, and most particularly in the oxidation state III, has been the subject of much confusion and misinterpretation. Only recently, as a result of careful reinvestigations[2–10] of older claims,[11–14] with the indispensible aid of infrared and X-ray diffraction data, have certain basic facts become clearly established. These will be very briefly summarized in order to establish clearly the context in which the new results to be reported here should be viewed.

A.—Re(II) complexes are relatively rare. The ones which seem to be firmly established are of the types $[ReX_2(P(C_6H_5)_3)_2]$, where X = Cl, I[2], and $[ReX_2(LL_2)]$, where the ligand is either a diphosphine[2] or a diarsine[15] and X is a halide ion. Essentially nothing is known regarding the structures of these compounds.

The Re(II) arsine complexes, $[ReX_2(QAS)]$ [X = Cl, Br) and $[ReX_2(TAS)]$ (X = Cl, Br, I), in which QAS and TAS are tetra- and triarsine ligands, respectively, have also been prepared.[16] The former appear to be six-coordinate and the latter five-coordinate; both series are remarkable in resisting oxidation.

B.—Re(III) complexes are of several structural types.

(1) There are many[4,7] of the type $Re_2X_9L_3$ (often written in earlier literature as ReX_3L, $Re_2X_6L_2$, or $[ReX_3L]_n$). These are derived directly from rhenium(III) chloride or bromide in which the persistent[17] Re_3X_9 unit is the main structural feature.[5,7] References in older literature to $ReCl_3$ and Re_2Cl_6 (even recently[3]) pertain to Re_3Cl_9, the only known form of anhydrous rhenium(III) chloride.

(2) Closely related to these are the pure halo complexes which also contain the Re_3X_9 group.[6,7,20–24] These contain anions of the types $[Re_3X_{12}]^{3-}$, $[Re_3X_{11}]^{2-}$, and $[Re_3X_{10}]^{-}$.

In addition to this large group of well-characterized Re(III) complexes based on the Re_3X_9 groups, there are several other classes, each represented, so far, by only a few examples, and, with the exception of the $[Re_2X_8]^{2-}$ type, not definitively characterized with respect to structure.

(3) Only two complexes of the type $ReCl_3L_3$, namely that in which L_3 represents three $P(C_2H_5)_2C_6H_5$ groups and that in which L_3 represents one $P(C_2H_5)_2C_6H_5$ and one $1,2\text{-}C_2H_4(P(C_6H_5)_2)_2$ group have been well-established.[2] For the former, the dipole moment indicates a *trans* octahedral structure.[2]

(4) Several complexes of the type $[ReX_2(LL)_2]Y$, where X = halide, Y = halide or ClO_4, and LL represents a diphosphine[2] or diarsine, have been reported.[15] The $[Re(diars)_2X_2]^+$ ions can be oxidized by additional X_2 (X = Cl, Br) to the $[Re(diars)_2X_4]^+$ ions, which are

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(1) Supported by the U. S. Atomic Energy Commission.

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(7) F. A. Cotton, S. J. Lippard, and J. T. Mague, *ibid.*, **4**, 508 (1965).

(8) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *ibid.*, **4**, 326 (1965).

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(14) G. K. Babeshkina and V. G. Tronev, *Zh. Neorgan. Khim.*, **7**, 715 (1962); *Russ. J. Inorg. Chem.*, **7**, 108 (1962), and earlier references cited therein.

(15) N. F. Curtis, J. E. Fergusson, and R. S. Nyholm, *Chem. Ind.* (London), 625 (1958).

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(17) Recent mass-spectrographic studies of the chloride[18,19] and the bromide[18] have shown that the Re_3X_9 group is by far the major species even in the gas phase at 500–700°.

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(21) B. H. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc.*, 116 (1963).

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(23) M. Elder and B. R. Penfold, *ibid.*, **205**, 276 (1965).

(24) B. H. Robinson and J. E. Fergusson, *J. Chem. Soc.*, 5683 (1965).

apparently eight-coordinate.[25] Another eight-coordinate Re(V) complex is the $[Re(CN)_8]^{3-}$ ion.[26]

(5) The only well-characterized complex of the type $ReCl_3L_2$, for which such a formula is still claimed[8] after various reinvestigations, is $ReCl_3(OP(C_6H_5)_3)_2$. This is prepared[3] in a roundabout way, so that its origin in Re_3Cl_9 does not imply that the trimeric unit should necessarily remain. However, the only evidence that it is not in fact the corresponding Re(V) oxo complex, $ReOCl_3(OP(C_6H_5)_3)_2$, is the absence of any band attributable to Re=O in the range 780–1000 cm.$^{-1}$. Since the Re=O bands of $ReOX_4^-$ ions have recently been found[27] as high as 1010 cm.$^{-1}$, it can be said that the non-oxo nature of this substance is still not absolutely certain.

Diamagnetic [Re(diarsine)Cl_3] is briefly mentioned.[28] From the diamagnetism it is concluded that the compound is probably a trigonal bipyramid.

(6) The two ions[8,9] $[Re_2Cl_8]^{2-}$ and $[Re_2Br_8]^{2-}$ as well as the binuclear halo carboxylate complexes[29] $[Re_2(RCO_2)_4X_2]$ can be prepared in high yield by ligand exchange from the $Re_2X_8{}^{2-}$ compounds[8] or in very low yield from rhenium(III) chloride. The $[Re_2X_8]^{2-}$ ions are themselves prepared[8] by reduction of ReO_4^- in aqueous HX with H_3PO_2 or H_2. In all of these species the existence of a Re–Re *quadruple* bond has been postulated.[30]

C.—Aside from the hexahalo complexes, $[ReX_6]^{2-}$, no well-established Re(IV) complexes have been reported in detail. Malatesta[31] has, however, given a preliminary report of the isolation of $ReCl_4(P(C_6H_5)_3)_2$.

D.—The Re(V) complexes are of five main types.[32]

(1) The $ReOX_3L_2$ compounds,[2,3] mostly derived from ReO_4^- by treatment with HX and L (where L is a phosphine or arsine) in an alcohol. Presumably, the phosphine or arsine reduces ReO_4^- to ReO^{3+}, forming R_3PO or R_3AsO.

The compounds $[ReOX_3(TAS)]$ (X = Cl, Br; TAS = a triarsine) have also been reported,[16] but it is uncertain whether they are six- or seven-coordinate.

(2) The $ReO(OR)X_2L_2$ compounds,[2,3] which can be obtained directly from ReO_4^-, under the same general conditions as for the $ReOX_3L_2$ complexes except for the strict exclusion of water or from the $ReOX_3L_2$ complexes by solvolysis with ROH.

(3) The $[ReOX_4]^-$ and $[ReOX_4L]^-$ salts[27] obtained by reduction of ReO_4^- in methanol–H_2SO_4 with zinc, followed by treatment with HX and L. By treating these with phosphines, they are converted to those of type D(1).

(4) The dioxo[32] complexes, $[ReL_4O_2]^+$; the oxo-hydroxy[33] complexes, $[ReL_2Cl_2O(OH)]$; and the dihydroxy[33] complexes $[ReL_2Cl_2(OH)_2]^+$ and $[ReCl_4(OH)_2]^-$, all of which apparently contain a linear O–Re–O group. The ultraviolet and infrared spectra of the last complex may indicate that it is in fact[34] $[ReCl_4O(H_2O)]^-$.

(5) The RN=Re(V) and N≡Re(V) complexes were recently discovered by Chatt, *et al.*[35]

The work described in this paper is an investigation of the complexes which can be obtained by reaction of the $[Re_2X_8]^{2-}$ ions with phosphine and diphosphine ligands.

Experimental

1,2-Bis(diphenylphosphino)ethane, hereafter abbreviated diphos, was prepared by reaction of $(C_6H_5)_2PLi$ with $ClCH_2CH_2Cl$.[36]

Analyses were performed by S. M. Nagy, Massachusetts Institute of Technology, and Galbraith Microanalytical Laboratories, Knoxville, Tenn. Neutron activation analyses for oxygen were done by General Atomics, San Diego, Calif. We have been informed by this company that "due to the possibility of interfering spectra, no pre-established limit of sensitivity can be guaranteed" for those oxygen analyses, but that "in all cases ...... firm upper limits (on O content) will be established (by the results) even when the presence of the element at these levels cannot be conclusively shown." In other words, there cannot be more oxygen present than what is indicated and, conceivably, there could be none even when a small positive result is obtained.

Infrared spectra were recorded in the range 400–4000 cm.$^{-1}$ using a Perkin-Elmer 337 spectrometer. Ultraviolet and visible spectra were obtained with Beckman DU and Cary Model 14 spectrophotometers. Conductivities were measured at 23 ± 2° with a commercial Wheatstone bridge circuit.

$[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$.—Potassium perrhenate, 2.0 g., and sodium chloride, 2.0 g., were heated in 40 ml. of 50% aqueous hypophosphorous acid for 10 hr. at about 90°. To the resulting dark solution was added 4.0 g. of tetra-*n*-butylammonium bromide in 75 ml. of 6 *N* HCl, and heating was continued for 12 hr. The hot solution was then filtered, yielding the crude blue product which was washed with 20 ml. of 6 *N* HCl and then three 20-ml. portions of ethanol. After drying under vacuum for 4 hr., this material is sufficiently pure to be used in the preparative reactions described below. It may, however, be recrystallized by dissolving it in 200 ml. of methanol, filtering, adding 50 ml. of 12 *N* HCl, and evaporating the methanol on a steam bath; yield 40%.

$[(n\text{-}C_4H_9)_4]_2[Re_2Br_8]$.—To a solution of 1.5 g. of raw $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ in 200 ml. of methanol was added 50 ml. of concentrated HBr. Evaporation of the methanol on a steam bath yielded olive-green crystals of the bromide dimer; yield 98%.

$[ReCl_3P(C_6H_5)_3]_n$.—To a solution of 1.0 g. of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ (0.877 mmole) in 200 ml. of methanol, containing 5 ml. of 6 *N* HCl to repress hydrolysis, was added 0.5 g. of triphenylphosphine (1.91 mmoles). This solution was stirred for 30 min. The green powder which had precipitated at the end of this time was filtered from the colorless mother liquor, washed with 30 ml. each of acetone, ethanol, benzene, and ether, and then dried at 80° under vacuum for 4 hr. This compound is insoluble in all common solvents; yield 98%.

Anal. Calcd. for $C_{18}H_{15}PReCl_3$: C, 38.95; H, 2.72; P, 5.59; Cl, 19.17. Found: C, 38.70; H, 2.90; P, 5.34; Cl, 19.12.

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[28] R. S. Nyholm, 10th Solvay Conference, 1956, p. 271.

[29] F. Taha and G. Wilkinson, *J. Chem. Soc.*, 5406 (1963).

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[31] L. Malatesta, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 475.

[32] There are a few other well-characterized Re(V) complexes which do not fall within the following classes; see for example ref. 3 and 29.

[33] J. H. Beard, J. Casey, and R. K. Murmann, *Inorg. Chem.*, **4**, 797 (1965).

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[ReBr$_3$P(C$_6$H$_5$)$_3$]$_n$.—This reddish brown compound was prepared in a manner analogous to that for the chloride except that the product was washed with acetone until the washings were colorless. Like the chloride, this compound is insoluble in all common solvents; yield 98%.

Anal. Calcd. for $C_{18}H_{15}PReBr_3$: C, 31.51; H, 2.19; P, 4.50; Br, 34.84; O, 0.0. Found: C, 31.53; H, 2.43; P, 4.46; Br, 32.9; O, 0.75. The reason for the low bromine analysis is unknown.

[Re(diphos)Cl$_3$].—Stirring 0.5 g. of [(n-C$_4$H$_9$)$_4$N]$_2$[Re$_2$Cl$_8$] (0.438 mmole) with 0.5 g. of diphos (1.2 mmoles) in 60 ml. of acetonitrile yielded an insoluble pale purple precipitate after 2 hr. This precipitate was filtered, washed with ethanol (30 ml.), benzene (30 ml.), and diethyl ether (60 ml.), and then dried under vacuum at 80° for 4 hr.; yield 95%.

Anal. Calcd. for $C_{26}H_{24}P_2ReCl_3$: C, 45.18; H, 3.50; P, 8.96; Cl, 15.39; O, 0.0. Calcd. for $C_{26}H_{24}P_2ReCl_3O$: C, 44.16; H, 3.41; P, 8.78; Cl, 15.08; O, 2.26. Found: C, 45.11; H, 3.90; P, 8.83; Cl, 15.20; O, 0.44.

With the exception of dichloromethane, in which it is slowly oxidized by air, Re(diphos)Cl$_3$ is insoluble in all common solvents.

[Re(diphos)$_2$Cl$_2$]Cl.—Under a nitrogen atmosphere, a solution of 1.0 g. of [(n-C$_4$H$_9$)$_4$N]$_2$[Re$_2$Cl$_8$] (0.877 mmole) and 3.0 g. of diphos (7.55 mmoles) in 95 ml. of methanol and 5 ml. of concentrated HCl was refluxed for 48 hr. The solution was cooled to room temperature and filtered to remove small amounts of a green solid from the yellow solution. This solid was washed with methanol until the washings were colorless. The yellow washings and mother liquor were evaporated *at room temperature* to a volume of about 25 ml. The yellow-orange crystals which formed during this time were recovered, washed with a small amount of methanol (about 4 ml.) and then ether (20 ml.), and dried at 80° for 4 hr. under vacuum. The compound becomes orange upon drying, but dissolves in alcohols, acetone, acetonitrile, chloroform, or benzene to give yellow solutions; yield about 50%.

Anal. Calcd. for $C_{52}H_{48}P_4ReCl_3$: C, 57.32; H, 4.44; P, 11.39; Cl, 9.76. Found: C, 57.44; H, 4.53; P, 11.41; Cl, 9.82.

[Re(diphos)$_2$Cl$_2$]ClO$_4$.—To a solution of 0.2 g. of [Re(diphos)$_2$-Cl$_2$]Cl (0.183 mmole) in a minimum of methanol was added 0.1 g. of sodium perchlorate (0.82 mmole) dissolved in a small amount of methanol. As the solution was stirred, a flocculent yellow precipitate developed. After stirring for 30 min., this precipitate was filtered from the solution, washed with water (10 ml.), a small amount of ethanol (about 5 ml.), and ether (20 ml.), and then dried at 80° under vacuum for 4 hr.; yield 85%.

Anal. Calcd. for $C_{52}H_{48}P_4ReCl_3O_4$: C, 54.12; H, 4.19; P, 10.76; Cl, 9.22. Found: C, 54.21; H, 4.32; P, 10.44; Cl, 9.84.

The yellow product dissolves in acetone, alcohols, and acetonitrile to give yellow solutions.

[Re(diphos)$_2$Br$_2$]Br.—This compound was prepared from [(n-C$_4$H$_9$)$_4$N]$_2$[Re$_2$Br$_8$] and diphos using the procedure described for the preparation of the chloro analog except that the product was recrystallized from methanol by evaporation *at room temperature;* yield 30%.

Anal. Calcd. for $C_{52}H_{48}P_4ReBr_3$: C, 51.07; H, 3.96; P, 10.13; Br, 19.2. Found: C, 50.87; H, 4.13; P, 10.09; Br 18.90.

The deep red-orange crystals of the dried material dissolve in acetone, acetonitrile, chloroform, benzene, and alcohols to give yellow-orange solutions.

[Re(diphos)$_2$Br$_2$]ClO$_4$.—To the yellow solution and washings produced in the preparation of [Re(diphos)$_2$Br$_2$]Br was added 10 ml. of 70% aqueous perchloric acid. Evaporation *at room temperature* of this solution to a volume of about 10 ml. yielded orange crystals. These crystals were collected, washed with benzene (5 ml.) and ether (40 ml.), and then dried in air; yield 50%.

Anal. Calcd. for $C_{52}H_{48}P_4ReBr_2ClO_4$: C, 50.26; H, 3.98; P, 9.98; Br, 12.82. Found: C, 51.01; H, 4.13; P, 9.68; Br, 11.82.

The red-orange crystals of the dried material dissolved in alcohols, acetonitrile, and benzene to give yellow-orange solutions.

Re(diphos)Cl$_3$O.—A solution of 0.5 g. of Re(diphos)Cl$_3$ in 50 ml. of dichloromethane was refluxed for 24 hr. The pink solution gradually turned yellow, and at the end of this time pale green crystals were isolated by evaporation of the solution to about 5 ml. The crystals were collected by filtration, washed with ether (20 ml.) and light petroleum (20 ml.), and then dried in air; corrected m.p. 246–248°; yield 90%.

Anal. Calcd. for $C_{26}H_{24}P_2ReCl_3O$: C, 44.16; H, 3.41. Found: C, 44.48; H, 3.50.

The infrared spectrum showed absorptions very similar to those found in Re(diphos)Cl$_3$ except for peaks at 980 (s) and 940 (w) cm.$^{-1}$ in hydrocarbon oil or at 983 (s) and 932 (w) cm.$^{-1}$ in KBr.

[Re(diphos)$_2$O$_2$]ClO$_4$.—A solution of 0.5 g. of [(n-C$_4$H$_9$)$_4$N]$_2$-[Re$_2$Br$_8$] (0.344 mmole) and 1.5 g. of diphos (3.77 mmoles) in 100 ml. of methanol containing 4 ml. of 70% aqueous perchloric acid was refluxed for 1 hr. As the solution was slowly cooled to room temperature, an orange precipitate developed which was filtered, washed with benzene (5 ml.) and ether (40 ml.), and dried *in vacuo* at 80° for 4 hr.; yield 80%.

Anal. Calcd. for $C_{56}H_{48}P_4ReClO_6$: C, 56.02; H, 4.34; P, 11.13; Br, 0.0. Found: C, 55.75; H, 4.33; P, 10.90; Br, 0.70.

The yellow-orange crystals of the dry compound were soluble in methanol, acetonitrile, and acetone, giving yellow solutions.

[Re═N(C$_6$H$_5$)(diphos)Cl$_3$].—Refluxing 0.15 g. of Re(diphos)-Cl$_3$O in 25 ml. of benzene containing 4 ml. of aniline[35] for 18 hr. yielded a pale blue-green microcrystalline precipitate. This compound was washed with benzene (20 ml.) and ether (20 ml.), then dried *in vacuo* for 4 hr. at 80°.

Anal. Calcd. for $C_{32}H_{29}P_2NReCl_3$: C, 49.13; H, 3.74; N, 1.77; P, 7.92. Found: C, 49.30; H, 3.84; N, 1.94; P, 7.98.

Results

All of the phosphine complexes prepared in this work are listed in Table I along with certain of their physical properties. Figure 1 shows the infrared spectra of several of the complexes in the region of main interest. The spectra of the bromide complexes exhibit the same features as do their chloride analogs. In the region from ~1200 to 4000 cm.$^{-1}$ the spectra are all substantially identical with the spectra of the ligands themselves.

Triphenylphosphine Complexes.—A solution of [(n-C$_4$H$_9$)$_4$N]$_2$[Re$_2$X$_8$] (X = Cl or Br) in slightly acidic methanol reacts with triphenylphosphine to give insoluble powders with an empirical formula [ReX$_3$P(C$_6$H$_5$)$_3$]. With acetone, acetonitrile, dichloromethane, or molten triphenylphosphine no reaction is observed. In strongly acidic methanol, [(C$_6$H$_5$)$_3$PH]$_2$[Re$_2$X$_8$] is produced.

The infrared spectra of the [ReX$_3$P(C$_6$H$_5$)$_3$]$_n$ compounds show no peaks other than those attributable to coordinated P(C$_6$H$_5$)$_3$. In particular, no strong peaks which might be assigned to ReO or *trans*-OReO groups appear in the 750 to 1100 cm.$^{-1}$ range. In the visible reflectance spectra, one band, at 13,700 cm.$^{-1}$, appears in the spectrum of the chloride, while the bromide has absorptions at 12,600, 18,200 (sh), and 20,800 cm.$^{-1}$. Powder patterns of [ReBr$_3$P(C$_6$H$_5$)$_3$]$_n$ and Re$_3$Br$_9$[P(C$_6$H$_5$)$_3$]$_3$[7] obtained with Ni-filtered Cu radiation are distinctly different.

1,2-Bis(diphenylphosphino)ethane Complexes.—The product of the reaction of 1,2-bis(diphenylphosphino)-

TABLE I

SOME PROPERTIES OF THE COMPOUNDS PREPARED

	Compound	Color	Spectra		Misc.[d]
			Infrared bands,[a] cm.$^{-1}$	Visible bands, cm.$^{-1}$ (ϵ)	
1.	$[ReCl_3(P(C_6H_5)_3)]_n$	Green	...	13,700 (—[b])	Very insoluble
2.	$[ReBr_3(P(C_6H_5)_3)]_n$	Reddish brown	...	12,600 (—[b]) 18,200 sh 20,800 (—[b])	Very insoluble
3.	$[Re(diphos)Cl_3]_n$	Pale purple	...	18,000 (—[b])	Very insoluble
4.	$[Re(diphos)Cl_3O]$	Pale green	980 s (Re=O)	...	...
5.	$[Re(diphos)Cl_3NC_6H_5]$	Pale blue-green	...	...	...
6.	$[Re(diphos)_2Cl_2]Cl$	Yellow-orange	...	21,900 (990)[c] 23,200 (550)[c] 29,000 sh[c]	$\Lambda = 133$
7.	$[Re(diphos)_2Cl_2]ClO_4$	Yellow	625 w, 1095 s, vb (ClO_4)	21,700 (1190)[c] 23,200 (540)[c] ~30,000 sh[c]	$\Lambda = 136$
8.	$[Re(diphos)_2Br_2]Br$	Deep red-orange	...	21,600 (405)[c] 28,200 sh[c]	$\Lambda = 115$
9.	$[Re(diphos)_2Br_2]ClO_4$	Orange	628 m, 1093 s, b (ClO_4)	21,400 (350)[c] 27,600 sh[c]	$\Lambda = 120$
10.	$[Re(diphos)_2O_2]ClO_4$	Yellow-orange	789 s (O=Re=O, antisym) 635 w, 1103 s, b (ClO_4)	22,200 (<25, sh)[c]	$\Lambda = 121$

[a] Bands due to Re=O or ClO_4 only; s, strong; m, medium; w, weak; b, broad; v, very. [b] Mull spectra; no ϵ available. [c] From spectra of $\sim 10^{-3}$ *M* solutions in CH_3CN. [d] Λ represents molar conductance, ohm^{-1} cm.^{2}, of a $\sim$0.001 *M* solution in CH_3CN.

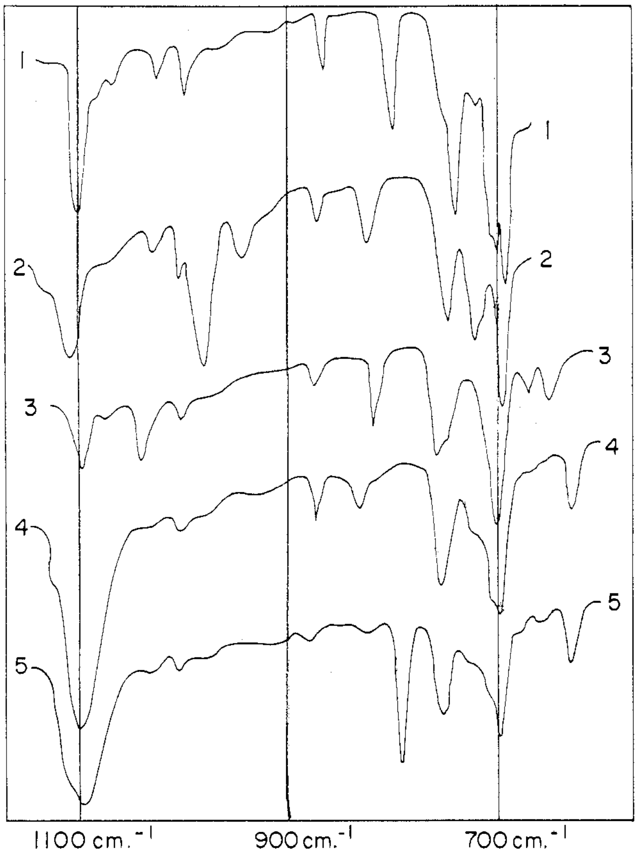

Figure 1.—Infrared spectra (as Nujol mulls): (1) Re(diphos)Cl_3, (2) Re(diphos)Cl_3O, (3) $[Re(diphos)_2Cl_2]Cl$, (4) $[Re(diphos)_2Cl_2]ClO_4$, (5) $[Re(diphos)_2O_2]ClO_4$.

ethane (diphos) with $[(n\text{-}C_4H_9)_4N]_2[Re_2X_8]$ (X = Cl or Br) is dependent upon the reaction medium and, in the presence of air, the temperature. With slightly more than 1 mole of diphos per mole of rhenium, the reaction depends on the solvent. In acetone the solution turns green and $[Re(diphos)_2Cl_2]Cl$ and $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ can be isolated. In acetonitrile or dichloromethane a pale purple powder, Re(diphos)Cl_3, separates rapidly. A dichloromethane solution of Re(diphos)Cl_3, exposed to air, gradually changes from pink to yellow, the change being accelerated by heat, and green Re(diphos)Cl_3O can be isolated from this solution. This green compound reacts with aniline in refluxing benzene to yield an insoluble blue-green imide complex, $[Re{=}N(C_6H_5)(diphos)Cl_3]$, of the type reported by Chatt, *et al.*[2,35]

With an excess of diphos in methanol $[(n\text{-}C_4H_9)_4N]_2[Re_2X_8]$ (X = Cl or Br) reacts to yield a yellow solution of $[Re(diphos)_2X_2]X$ which may be isolated by evaporation of the solvent at room temperature. Evaporation at elevated temperatures yields crystal mixtures whose infrared spectra indicate the presence of *trans*-dioxorhenium species. Addition of perchlorate to concentrated methanol solutions of $[Re(diphos)_2X_2]X$ precipitates the slightly less soluble $[Re(diphos)_2X_2]ClO_4$.

Refluxing $[(n\text{-}C_4H_9)_4N]_2[Re_2Br_8]$ with excess diphos in air in a methanol solution containing perchloric acid produces a yellow solution from which *trans*-$[Re(diphos)_2O_2]ClO_4$ may be isolated.

The infrared spectra (Table I, Figure 1) of the three compounds containing perchlorate ions show that these ions are not coordinated. Thus, the infrared-inactive a_1 Cl–O stretching mode is not observed at its normal position of about 935 cm.$^{-1}$, the t_2 OClO bending mode is observed unsplit at its normal position of ~630 cm.$^{-1}$, and the t_2 ClO stretching mode is observed at ~1090 cm.$^{-1}$ with no pronounced splitting. Considerably different results[37] are given by coordinated ClO_4^-.

Discussion

It may first be noted that the reaction conditions for the preparation of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ which are

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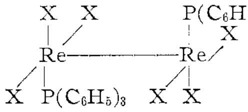
(37) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

reported here differ from those previously[8] described. They are superior in giving about twice the yield (~40%) of the desired product. Since the exchange reaction which produces $[Re_2Br_8]^{2-}$ from $[Re_2Cl_8]^{2-}$ proceeds in virtually quantitative yield, the preparation of both these ions has now been significantly improved.

The $[ReX_3P(C_6H_5)_3]_n$ Compounds.—While we have not proved conclusively the nature of these complexes, it seems likely that they are dimers, probably with the structure I, derived from the $[Re_2X_8]^{2-}$ ions by substitution. They are not likely to be monomers, and they are not the same as the cyclic trimers previously characterized.[4,7] While the electronic spectra observed by reflectance are consistent with structure I they do not provide positive evidence for it, and therefore we must admit that an infinite polymeric structure such as II, and perhaps other structures, are possible, though, in our view unlikely. The insolubility of the compounds makes it impossible to obtain more definitive evidence, but attempts to prepare more soluble analogs using other phosphines are in progress.



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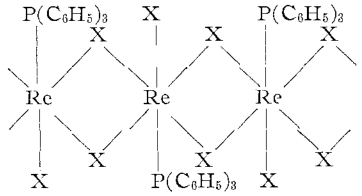

II

Re(diphos)Cl$_3$ and Derivatives.—This compound is of exceptional interest because, as noted in the Introduction, of all compounds previously reported with stoichiometry $ReCl_3L_2$, there are only two which have not subsequently been shown to be $ReOCl_3L_2$ compounds. In the present case there are several lines of evidence supporting the formulation as an Re(III) complex.

(1) Direct oxygen analysis gives an upper limit (see remarks at the beginning of the Experimental section) of 0.22 O/Re. Moreover, the H analyses on the same sample are a little high, so that the presence of traces of H_2O, perhaps adsorbed on the surface, seems a satisfactory explanation of the small quantity of oxygen indicated.

(2) The infrared has no absorption attributable either to Re=O or to P=O from 750 to 1200 cm.$^{-1}$ (Figure 1).

(3) An authentic Re(diphos)Cl$_3$O has been prepared from Re(diphos)Cl$_3$ and is a recognizably different substance having a strong Re=O band in the infrared (see Figure 1). The Re(diphos)Cl$_3$O we have isolated is green and must be one of the two *cis* isomers possible.[2] Chatt and Rowe[2] report a compound of the same stoichiometry which is blue. Presumably, this is the other isomer. The apparent difference, 4 cm.$^{-1}$, in the Re=O frequencies is probably without significance since they were obtained in separate experiments, but Chatt and Rowe have reported differences of only 1 and 9 cm.$^{-1}$ between *cis* and *trans* isomers of such compounds, so this is apparently a poor criterion of structural difference. Our compound has a melting point (with decomposition) which differs by about 12° from that reported for the blue isomer.

(4) Re(diphos)Cl$_3$O reacts with aniline to give Re(diphos)Cl$_3$NC$_6$H$_5$, which in turn supports the formulation of the oxo compound. On examining the infrared spectrum of this compound, we confirm the observation of Chatt, *et al.*,[28] that there is no obvious Re=N stretching band.

As to the structure of Re(diphos)Cl$_3$ we have no evidence. The insolubility of the substance prevents making molecular weight measurements which could distinguish between the two most obvious possibilities, *viz.*, a five-coordinate monomer and a chlorine-bridged, six-coordinate dimer.

[Re(diphos)$_2$O$_2$]ClO$_4$.—This compound contains the fourth *trans*-$[Re^VO_2L_4]$ or *trans*-$[Re^VO_2(LL)_2]$ species to be reported and characterized by its infrared spectrum, the others[3] being $[ReO_2(py)_4]^+$, $[ReO_2(en)_2]^+$, and $[ReO_2(CN)_4]^{3-}$. Its single Re=O band, due to the antisymmetric stretching mode of O=Re=O, at 790 cm.$^{-1}$ can be compared with those found in the others at 818 ± 6, 816 ± 3, and 780 cm.$^{-1}$, respectively.

[Re(diphos)$_2$X$_2$]Y Compounds.—The compound with X = Y = Cl has previously been prepared[2] and several analogous diarsine derivatives are also known.[15] The molar conductances show that in acetonitrile solution all four compounds described here are 1:1 electrolytes. Moreover, the electronic spectra of the corresponding pairs of compounds, with Y = X, ClO$_4$, are essentially identical, and the infrared spectra of the solid compounds show that the perchlorate ions are uncoordinated. The assumption that six-coordinate $[Re(diphos)_2X_2]^+$ cations must be present in the solid compounds as well as in solution seems a very reasonable one.

Concluding Remarks.—The work described here shows that on treatment of the $[Re_2X_8]^{2-}$ ions with phosphines under conditions where oxidation is not promoted, one of three types of Re(III) complex may be obtained. Of particular interest are those in which the Re–Re bond is apparently retained. Under conditions favoring oxidation Re^V=O and O=Re^V=O complexes can be formed. These results are entirely consistent with the idea[8] that the starting compounds contain Re(III).