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Chemistry of Rhenium(V) Chloride

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Received April 6, 1970

The reaction of rhenium(V) chloride and triphenylphosphine in acetone, acetonitrile, and benzene has been investigated. The mode of reaction has been found to be dependent upon the age of the rhenium(V) chloride, the solvent, and the amount of water present in the solvent. The reaction in acetone led to the isolation of four products: $ReOCl_3[P(C_6H_5)_3]_2$, $ReCl_4[P(C_6H_5)_3]_2$, $[CH_3COCH_2C(CH_3)_2P(C_6H_5)_3]ReCl_5P(C_6H_5)_3$, and a mixture of $[CH_3COCH_2C(CH_3)_2P(C_6H_5)_3]_2Re_2Cl_9$ and $[CH_3COCH_2C(CH_3)_2P(C_6H_5)_3]_2Re_2Cl_8$. The products isolated in benzene were $[ReCl_3P(C_6H_5)_3]_x$ and $[(C_6H_5)_3PH]_2Re_2Cl_9$, while in acetonitrile only $ReCl_4[P(C_6H_5)_3]_2$ was isolated. The nature of the products, mode of formation, and spectral data will be discussed.

Introduction

In recent years the chemistry of nonachlorotrirhenium(III) and β-rhenium(IV) chloride have been extensively investigated.[1,2] However, the chemistry of rhenium(V) chloride has received little attention, probably due to its hydrolytic instability. In 1964, Johnson, Lock, and Wilkinson[3] reported its reactions with triphenylphosphine in dichloromethane or dry acetone and with pyridine in wet acetone. The former yielded $[ReCl_4P(C_6H_5)_3]_x$; the latter, $[ReO_2(C_5H_5N)_4]Cl \cdot 2H_2O$ and a product later identified as $Re_2O_3Cl_4(C_5H_5N)_4$.[4] Cotton, *et al.*,[2] have been unable to repeat the latter preparation procedure. Later the reaction of rhenium(V) chloride and triphenylphosphine in acetone was reported to form two isomers of the compound $ReCl_3P(C_6H_5)_3 \cdot 2C_3H_6O$ and $ReOCl_3[P(C_6H_5)_3]_2$.[5] The reaction of rhenium(V) chloride and anhydrous acetonitrile yields $ReCl_4(CH_3CN)_2$[6] and with concentrated hydrochloric acid, $ReOCl_5^{2-}$.[7] Its reaction with a series of oxygen donors led to the isolation of compounds of the type $ReCl_4L_2$, where L = dioxane and tetrahydrofuran.[8] In a recent paper, Allen, *et al.*,[9] have reported the reaction of rhenium(V) chloride and water in acetone to yield the dinuclear species $Re_2Cl_8^{2-}$.

The purpose of this investigation was to learn more about the chemistry of rhenium(V) chloride through its reaction with triphenylphosphine. This reactant was chosen since it had been extensively used in previous studies with rhenium compounds and would expedite product identification. Also, its reaction with rhenium(V) chloride had led to conflicting results. The suggestion of a trinuclear rhenium(V) cation $Re_3Cl_{12}^{3+}$ with stability comparable to Re_3Cl_9[10] led us to investigate the possibility of cluster arrangements in the higher oxidation states. Such a study would be aided by knowledge of behavior of rhenium(V) chloride in solution. By a variation in the nature of the solvent and the use of triphenylphosphine, known to be present in many rhenium(V) compounds,[1] we hoped to attain the goal. We wish to report the findings which differ significantly from previous work and substantially increase our knowledge of rhenium(V) chloride.

Experimental Section

Materials.—Proton nmr were recorded on a Varian A-60A using CD_3CN or $CDCl_3$ as the solvent. Infrared spectra were obtained as KBr disks or as Nujol mulls on KBr plates (4000–400 cm^{-1}) and between polythene sheets (400–250 cm^{-1}) on a Perkin-Elmer Model 521 grating infrared spectrophotometer. Ultraviolet and visible spectra were recorded on a Beckman DK-2A recording spectrophotometer. Molecular weight determinations were performed on a Mechrolab 301A vapor pressure osmometer in CH_3CN. Conductivities were determined using a Fisher Model 16B2 conductivity bridge. X-Ray powder patterns were obtained from a Picker biplane diffractometer and Cu Kα radiation with a nickel filter. Carbon and hydrogen analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn., or the analyst at South Dakota State University. Rhenium and chlorine content were determined by standard methods.

Rhenium(V) chloride was prepared by a modified procedure of Hurd and Brimm.[11] Triphenylphosphine, Alfa Inorganics, was used as received. Anhydrous acetone was obtained by distillation from P_4O_{10} onto Linde 5A molecular sieves. Other solvents were dried by standard procedures.[12] Acid-washed alumina was prepared by washing Baker basic alumina with concentrated hydrochloric acid, washing repeatedly with distilled water, and drying at 250°. All reactions were carried out in an inert-atmosphere box under prepurified nitrogen.

Reaction of Rhenium(V) Chloride and Triphenylphosphine in Acetone.—Rhenium(V) chloride, 1.3 g (3.6 mmol), was dissolved in 25 ml of acetone. The solution was initially red-brown, but as more rhenium(V) chloride dissolved the solution became green. Addition of triphenylphosphine, 3.9 g (14.9 mmol), in 10 ml of acetone resulted in an immediate darkening of the solution. Green crystals soon appeared and after 30 min the solution was red-brown. After standing overnight, the reddish crystals were isolated by filtration, washed with acetone, and dried. Most of the crystals dissolved in chloroform, leaving a small amount of yellow solid identified as $ReOCl_3[P(C_6H_5)_3]_2$ by the infrared spectrum. The red solution was passed down a

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(1) J. E. Fergusson, *Coord. Chem. Rev.*, **1**, 460 (1966).

(2) F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, **6**, 223 (1967).

(3) N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *J. Chem. Soc.*, 1054 (1964).

(4) N. P. Johnson, F. I. M. Taha, and G. Wilkinson, *ibid.*, 2514 (1964).

(5) D. E. Grove and G. Wilkinson, *ibid.*, *A*, 1224 (1966).

(6) G. Rouschias and G. Wilkinson, *ibid.*, *A*, 489 (1968).

(7) R. Colton, *Aust. J. Chem.*, **18**, 435 (1965).

(8) E. A. Allen, N. P. Johnson, D. T. Rosevear, and W. Wilkinson, *J. Chem. Soc. A*, 778 (1969).

(9) E. A. Allen, N. P. Johnson, D. T. Rosevear, and W. Wilkinson, *Inorg. Nucl. Chem. Lett.*, **5**, 239 (1969).

(10) R. Colton and R. L. Martin, *Nature (London)*, **205**, 239 (1965).

(11) L. C. Hurd and E. Brimm, *Inorg. Syn.*, **1**, 180 (1939).

(12) J. A. Riddick and E. E. Toops, Jr., "Technique of Organic Chemistry," Vol. 7, 2nd ed, Interscience, New York, N. Y., 1967.

25-cm alumina column giving a faint yellow band, a red band, and a decomposition band at the top of the column indicative of the presence of $ReOCl_3[P(C_6H_5)_3]_2$. Dark red crystals, obtained by concentration of the red fraction, were isolated by filtration, washed with chloroform, and dried. The yield was 0.76 g (25%) of $ReCl_4[P(C_6H_5)_3]_2$. The infrared spectrum is the same as obtained previously.[13] *Anal.* Calcd for $C_{36}H_{30}P_2ReCl_4$: C, 50.76; H, 3.53. Found: C, 50.81; H, 3.87.

The mother liquor was removed from the drybox and passed down an alumina column with the order of elution of bands from the column: red, yellow, and purple. The purple material repeatedly failed to elute completely from the column when using acetone, but the addition of acetonitrile resulted in a greater percentage of elution. A blue band remained on the column despite the usage of various eluents. Separation was not possible with other types of column packings. The fractions were collected according to the color and concentrated to one-third the original volume on a rotary evaporator. Diethyl ether was added to induce crystallization. A solid was isolated from the yellow fraction by filtration, washed with diethyl ether, and dried at 1 mm and 80°. This procedure gave 0.44 g (12.6%) of yellow $(DOTP)ReCl_5P(C_6H_5)_3$. (DOTP is the abbreviation previously designated for the 1,1-dimethyl-3-oxobutyltriphenylphosphonium cation.[14]) *Anal.* Calcd for $C_{42}H_{41}P_2ReOCl_5$: C, 51.10; H, 4.20; Cl, 17.99. Found: C, 50.78; H, 4.31; Cl, 17.22. The molecular weight is 1083 (calcd 987). The infrared spectrum showed bands at 3410 (w), 3058 (w), 2980 (vw), 1960 (vw), 1910 (vw), 1815 (vw), 1710 (s), 1610 (vw), 1585 (w), 1575 (vw), 1483 (s), 1436 (vs), 1388 (w), 1370 (w), 1360 (w), 1340 (w), 1190 (w), 1180 (w), 1172 (sh), 1130 (w), 1100 (s), 1092 (sh), 1070 (sh), 1030 (w), 999 (m), 940 (w), 850 (vw), 750 (s), 720 (m), 695 (vs), 675 (sh), 585 (w), 540 (sh), 535 (s), 520 (m), 499 (m), 450 (w), 341 (w), 311 (vs), and 290 cm^{-1} (w). The purple fraction gave 0.012 g of a mixture of $(DOTP)_2Re_2Cl_9$ and $(DOTP)_2Re_2Cl_8$. *Anal.* Calcd for $C_{48}H_{52}O_2P_2Re_2Cl_9$: C, 40.76; H, 3.71; Re, 26.3. Calcd for $C_{48}H_{52}O_2P_2Re_2Cl_8$: C, 41.81; H, 3.80; Re, 27.0. Found: C, 41.04; H, 3.77; Re, 26.17. A molar conductivity of 258 in acetonitrile is indicative of a 2:1 electrolyte.[15] Prompt work-up of the reaction mixture improves the amount of the $Re_2Cl_9^{2-}$ ion. This was determined by the infrared and visible spectra as well as the X-ray powder pattern.

The product consistently had high carbon and hydrogen analyses which fell into two groups—one with approximate values of 42.5% carbon and 4.0% hydrogen and the other with 43.0% carbon and 4.3% hydrogen. These values are in good agreement with the compounds $(DOTP)_2Re_2Cl_8 \cdot C_3H_6O$ (calcd: C, 42.63; H, 4.07) and $(DOTP)_2Re_2Cl_8 \cdot 2C_3H_6O$ (calcd: C, 43.38; H, 4.31). The X-ray powder patterns were almost identical with that of pure $(DOTP)_2Re_2Cl_8$, while the infrared spectrum indicated the presence of coordinated acetone with a carbonyl stretching frequency at 1690 cm^{-1}.

The weights of the products represent approximately 50% of the rhenium present as $ReCl_5$. The majority of this rhenium was lost on the chromatography column as the fractions rarely separated completely and the tails of each fraction were discarded.

Reaction of Rhenium(V) Chloride and Triphenylphosphine in Wet Acetone.—Rhenium(V) chloride, 1.2 g (3.2 mmol), was dissolved in 25 ml of acetone and 3 drops of deoxygenated water was added. To this solution was added 3.3 g (12.7 mol) of triphenylphosphine in 10 ml of acetone which contained 2 drops of water. After standing for 1 hr, 0.90 g of $ReOCl_3[P(C_6H_5)_3]_2$ was isolated by filtration, washed with acetone, and dried. Recrystallization from methylene chloride gave 0.75 g (28.2%) of pure product. *Anal.* Calcd for $C_{36}H_{30}P_2ReOCl_3$: C, 51.99; H, 3.61; Re, 22.8; Cl, 13.1. Found: C, 51.80; H, 3.82; Re, 23.64; Cl, 13.27.

Work-up of the purple mother liquor was the same as described above and yielded 0.02 g (0.6%) of $ReCl_4[P(C_6H_5)_3]_2$, 0.49 g (13.2%) of $(DOTP)ReCl_5P(C_6H_5)_3$, and 0.03 g of the purple mixture.

Reaction of "Aged" Rhenium(V) Chloride and Triphenylphosphine in Acetone.—Rhenium(V) chloride, 1.35 g (3.7 mmol), was aged by allowing it to stand uncapped in the drybox for 2 days prior to use. Dissolution in 25 ml of acetone gave the same red-brown coloration observed with fresh rhenium(V) chloride in acetone. To this was added a solution of triphenylphosphine, 4.0 g (16.3 mmol), in 10 ml of acetone. The reaction yielded results very similar to those in wet acetone, including 0.382 g (10.6%) of $(DOTP)ReCl_5P(C_6H_5)_3$ and 0.052 g of the purple mixture.

The X-ray powder pattern of "aged" rhenium(V) chloride indicates a loss of crystallinity but does not show lines attributable to compounds such as β-$ReCl_4$ or $ReOCl_4$. The infrared spectrum does not contain an Re=O band. Further work is under way to elucidate its composition.

Preparation of $(DOTP)ReCl_5P(C_6H_5)_3$.—To a solution of 0.2 g of $[(C_6H_5)_3PH]ReCl_5P(C_6H_5)_3$[16] dissolved in 35 ml of methylene chloride was added 0.5 g of $(DOTP)HCl_2$ in 35 ml of ethanol. The resulting solution was concentrated to 40 ml, without heat, on a rotary evaporator. Approximately 20 ml of hexane was added and the solution was further evaporated until crystallization began. The yellow solid was isolated by filtration, washed with ethanol and diethyl ether, and dried. The yield was 0.15 g (68%) of $(DOTP)ReCl_5P(C_6H_5)_3$. Product identification was made by elemental analyses and a comparison of the infrared spectrum to that of an authentic sample.

Preparation of $(DOTP)_2Re_2Cl_9$.—The method of preparation was the same as that employed for the preparation of $(DOTP)ReCl_5P(C_6H_5)_3$. The solution slowly turned deep violet and diethyl ether was added to induce crystallization. Violet crystals of $(DOTP)_2Re_2Cl_9$ were isolated by filtration, washed with ether, and dried, giving a 0.4-g (84%) yield. The infrared spectrum showed bands at 3410 (w), 3060 (w), 2980 (w), 2930 (vw), 2000 (vw), 1910 (vw), 1882 (vw), 1715 (vs), 1620 (vw), 1580 (m), 1570 (sh), 1480 (s), 1450 (w), 1432 (vs), 1410 (vw), 1385 (w), 1370 (vw), 1350 (w), 1330 (w), 1310 (vw), 1265 (vw), 1185 (w), 1160 (w), 1120 (w), 1100 (vs), 1070 (vw), 998 (m), 935 (w), 840 (vw), 745 (s), 718 (vs), 695 (vs), 685 (sh), 660 (w), 610 (w), 575 (m), 530 (vs), 498 (m), 425 (vw), 323 (vs), 310 cm^{-1} (sh). *Anal.* Calcd for $C_{48}H_{52}P_2O_2Re_2Cl_9$: C, 40.76; H, 3.71. Found: C, 40.93; H, 4.01. The molecular weight is 1346 (calcd 1414).

This method of synthesis is not good, for, repeatedly, further reaction took place to yield a mixture of the $Re_2Cl_9^{2-}$ and $Re_2Cl_8^{2-}$ salts. The use of $[(C_4H_9)_4N]_2Re_2Cl_9$ also results in the formation of a mixture.

Preparation of $(DOTP)_2Re_2Cl_8$.—This compound can be prepared by the method described above or by the reaction of β-$ReCl_4$ and $(DOTP)HCl_2$ in an acetone solution containing concentrated hydrochloric acid.[17] The infrared spectrum consisted of the same gross features as those listed for $(DOTP)_2Re_2Cl_9$, but with the carbonyl stretching frequency at 1720 cm^{-1} and the asymmetric rhenium–chlorine stretching mode at 330 cm^{-1}. *Anal.* Calcd for $C_{48}H_{52}P_2O_2Re_2Cl_8$: C, 41.81; H, 3.80. Found: C, 41.77; H, 4.02. The molecular weight is 1307 (calcd 1414).

Reaction of Rhenium(V) Chloride and Triphenylphosphine in Anhydrous Acetonitrile.—The addition of rhenium(V) chloride to anhydrous acetonitrile resulted in the formation of a deep red-orange solution. Upon the addition of triphenylphosphine, the solution became light orange. On standing, red crystals of $ReCl_4[P(C_6H_5)_3]_2$ were present. They were isolated by filtration, washed with acetone, and dried. Identification was made by comparison of the infrared spectrum to that of an authentic sample.

Reaction of Rhenium(V) Chloride and Triphenylphosphine in Benzene.—Rhenium(V) chloride, 0.33 g (0.9 mmol), was added to 75 ml of benzene. After intermittent swirling and standing, the undissolved $ReCl_5$ (0.19 g) was isolated by filtration and 1.00

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[13] G. Rouschias and G. Wilkinson, *J. Chem. Soc. A*, 465 (1966).

[14] H. Gehrke, Jr., G. Eastland, and M. Leitheiser, *J. Inorg. Nucl. Chem.*, **32**, 867 (1970).

[15] R. S. Drago and D. W. Herlocker, *Inorg. Chem.*, **7**, 1479 (1968).

[16] M. Freni, V. Valenti, and R. Pomponi, *Gazz. Chim. Ital.*, **94**, 521 (1964).

[17] H. Gehrke, Jr., unpublished results.

g (1.8 mmol) of triphenylphosphine was added to the filtrate. After standing overnight, 9.0 mg (4%) of violet $[(C_6H_5)_3PH]_2Re_2Cl_9$ was isolated by filtration, washed with benzene, and dried. The infrared spectrum showed bands at 3410 (vw), 3060 (w), 2920 (vw), 2385 (m) (ν_{P-H}), 1975 (vw), 1905 (vw), 1820 (vw), 1705 (w), 1610 (vw), 1590 (m), 1575 (sh), 1485 (m), 1440 (vs), 1340 (w), 1320 (w), 1190 (w), 1165 (w), 1110 (vs), 1075 (vw), 1030 (w), 999 (w), 925 (sh) (δ_{P-H}?), 900 (sh) (δ_{P-H}), 880 (m) (δ_{P-H}),[18] 745 (s), 720 (s), 690 (vs), 675 (sh), 610 (vw), 540 (m), 500 (vs), 430 (w), 400 (vw), 324 (vs), and 300 cm^{-1} (w). *Anal.* Calcd for $C_{36}H_{32}P_2Re_2Cl_9$: C, 35.44; H, 2.81. Found: C, 35.27; H, 3.28. The molar conductivity of 252 in acetonitrile is indicative of a 2:1 electrolyte.[15]

The yellow filtrate was concentrated on a rotary evaporator and 0.062 g (30%) of yellow-green $[ReCl_3P(C_6H_5)_3]_x$ was washed with diethyl ether and dried. The far-infrared spectrum showed bands at 343 (s) and 301 cm^{-1} (m). *Anal.* Calcd for $C_{18}H_{15}PReCl_3$: C, 38.95; H, 2.72. Found: C, 38.90; H, 3.47. Because of the insolubility of this compound, it must have formed during the concentration process which involved heating of the mother liquor.

Results and Discussion

The reaction of rhenium(V) chloride and triphenylphosphine in acetone is complex in nature and affords a varied set of compounds. The yield of these compounds, $ReOCl_3[P(C_6H_5)_3]_2$ (A), $ReCl_4[P(C_6H_5)_3]_2$ (B), $(DOTP)ReCl_5P(C_6H_5)_3$ (C), and a mixture of $(DOTP)_2Re_2Cl_9$ and $(DOTP)_2Re_2Cl_8$ (D), is dependent upon the "age" of the rhenium(V) chloride and the amount of water present in the acetone. In the absence of water, other than that produced in the formation of mesityl oxide, the products are predominantly B and C. The lack of oxygenated compounds seems to indicate that rhenium(V) chloride does not react with acetone in the same manner as other reactive pentahalides such as $MoCl_5$.[19] The addition of water to the acetone or the use of "aged" rhenium(V) chloride results in the formation of very little B, a consistent amount of C, and a greatly increased yield of A. The yield of D is increased, but it should be noted that it is a minor product in all cases. All salts identified in the present work have also been prepared by metathesis using the appropriate rhenium compound and $(DOTP)HCl_2$.

The mode of formation of the products is obviously complex, for Cotton and coworkers[20] have pointed out that the mechanism by which bimolecular ions are formed from mononuclear starting material is "entirely obscure." Allen and coworkers[9] have suggested that disproportionation of rhenium(V) chloride on hydrolysis in acetone follows the reaction scheme

$$7ReCl_5 + 12H_2O \longrightarrow 2Re_2Cl_9^{2-} + 3ReO_4^- + 17HCl + 7H^+$$

Mixture D is formed in accord with the equation, while A is known to be formed by the interaction of ReO_4^- and triphenylphosphine in the presence of hydrochloric acid.[21] The inability to form pure $(DOTP)_2Re_2Cl_9$ results from the facile reduction of the anion in acetone and hydrogen chloride.[2,9] Formation of C is more difficult to explain. If the reaction scheme is correct, C must either be prepared from the $Re_2Cl_9^{2-}$ or in a step prior to its formation, since the yield of A accounts for the total amount of ReO_4^- formed. Grove and Wilkinson[5] have suggested that the hydrolysis of rhenium(V) chloride produces $ReOCl_3$, which can react with triphenylphosphine in acetone to produce either A or D (incorrectly formulated as $ReCl_3P(C_6H_5)_3 \cdot 2(CH_3)_2CO$. Since both schemes give the same products it is not possible to determine the correct one. The formation of B and C as the major constituents in the absence of water is in line with the observation[6,8] that rhenium(V) chloride can be reduced to Re(IV) without oxygen abstraction or disproportionation. The consistent amount of C, with or without the presence of water, seems to indicate that a reaction scheme different from those discussed must be involved.

Johnson, Lock, and Wilkinson[3] have reported that the reaction of rhenium(V) chloride and triphenylphosphine in methylene chloride or dry acetone yields $[ReCl_4P(C_6H_5)_3]_x$, while in a later paper, Grove and Wilkinson[5] indicate that the reaction in acetone yields A and purple and green isomers of the composition $ReCl_3P(C_6H_5)_3 \cdot 2(CH_3)_2CO$. We have been unable to verify the latter formulations; however, the synthesis procedure and work-up, the presence of a carbonyl stretching mode at 1712 cm^{-1}, and the elemental analyses of the purple isomer lead us to believe that it is D. No compound fitting the description of the green isomer has been obtained.

In a previous paper,[14] we have discussed the formation and spectroscopic properties of compounds $(DOTP)HCl_2$ and $(DOTP)_2ReCl_6$. The former was prepared by the reaction of mesityl oxide, triphenylphosphine, and hydrogen chloride in diethyl ether, and the latter, by the reaction of $ReOCl_3[P(C_6H_5)_3]_2$ and hydrogen chloride in acetone or K_2ReCl_6, triphenylphosphine, and hydrogen chloride in acetone. It was proposed that the cation was formed by the acid-catalyzed condensation of acetone followed by a Michael addition of triphenylphosphine. In the present study, this mode of formation is possible when water is present in the acetone. In the initial absence of water, rhenium(V) chloride can serve as a Lewis acid in the condensation step. The speed of the reaction is somewhat surprising, as a work-up of the reaction media within 0.5 hr of the initial mixing results in the isolation of the compounds containing the cation. As the purification of the acetone could lead to the formation of some mesityl oxide, the acetone was checked by vpc and infrared techniques but did not indicate the presence of mesityl oxide.

While this work was under way, Allen and coworkers[8] reported the assignment of the vibrational modes present in the far-infrared spectrum of A and B, and we are in complete agreement with their assignments. The spectroscopic properties of the $DOTP^+$ ion, as the HCl_2^- and $ReCl_6^{2-}$ salts, have been discussed in detail previously[14] and are found to be the same in the present studies. Owing to the structural similarities,

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(18) P. M. Van Den Akker and F. Jellinek, *Recl. Trav. Chim. Pays-Bas*, **86**, 275 (1967).

(19) S. M. Horner and S. Y. Tyree, Jr., *Inorg. Chem.*, **1**, 122 (1962).

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

(21) J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 4019 (1962).

the only signficant differences arise from the nature of the anion. The ultraviolet and visible spectra of the $Re_2Cl_8^{2-}$ and the $Re_2Cl_9^{2-}$ salts are the same as that previously determined for these anions,[2,22] except for the enhanced character of the 353-mμ absorption. The ultraviolet and visible spectrum of C as recorded in methylene chloride is 290 (ϵ_0 4720), 320 (ϵ_0 2690), 385 (ϵ_0 2260), and 440 (ϵ_0 820) mμ. (DOTP)$ReCl_5P(C_6H_5)_3$ contains triphenylphosphine in two different environments, and this results in the P-sensitive mode[23] containing a strong band at 1100 cm^{-1} and a shoulder at 1092 cm^{-1}.

The elemental analyses of mixture D vary greatly and can be explained by the presence of coordinated acetone, as indicated by the carbonyl stretching mode at 1696 cm^{-1}, differing amounts of $Re_2Cl_9^{2-}$ and $Re_2Cl_8^{2-}$, and/or an impurity. One possible impurity is (DOTP)ReO_4, but it can be eliminated by the absence of rhenium–oxygen stretching modes indicative of ReO_4^-.[24] A second impurity might be C, due to incomplete separation on the chromatography column, while the third might be $(DOTP)_2ReCl_6$ whose anion might be formed from the $ReCl_5P(C_6H_5)_3^-$ ion or the reduction of the ReO_4^- ion.[25] X-Ray powder patterns have proved to be unsatisfactory except for the identification of dinuclear compounds, because of the complexity of the pattern due to the low symmetry of the compounds. In addition, there are modifications in the pattern of C, possibly indicating crystalline changes depending upon the recrystallization procedure. The ultraviolet and visible regions are useful in determining the presence of the dinuclear species, but their intense absorptions mask the absorption of $ReCl_6^{2-}$ or $ReCl_5P(C_6H_5)_3^-$ ions. The rhenium–chlorine asymmetric stretching mode (ν_3) has provided the most important method of determining the identity of the components of the mixture. The ν_3 mode in $(DOTP)_2Re_2Cl_8$ occurs at 294 cm^{-1}, in (DOTP)$ReCl_5P(C_6H_5)_3$ at 310 cm^{-1}, in $(DOTP)_2Re_2Cl_8$ at 330 cm^{-1}, and in $(DOTP)_2Re_2Cl_9$ at 323 cm^{-1}. The latter is in agreement with Cotton, *et al.*,[22] for this ion. (DOTP)$ReCl_5P(C_6H_5)_3$ usually contains weakly coordinated acetone as indicated by a carbonyl stretching frequency at 1698 cm^{-1}. All $LReCl_5P(C_6H_5)_3$ compounds, where L = $DOTP^+$, $(C_6H_5)_3PH^+$, and $(C_6H_5)_4As^+$, contain an additional band at 290 cm^{-1} which cannot presently be assigned to a specific vibrational mode. The infrared data, without the corroborative evidence furnished by the X-ray diffraction pattern, seem to indicate that the major impurity is C.

Rouschias and Wilkinson[6] have isolated $ReCl_4(CH_3CN)_2$ from the reaction of rhenium(V) chloride and acetonitrile and its subsequent reaction with triphenylphosphine to yield $ReCl_4[P(C_6H_5)_3]_2$. While we did not isolate the intermediate nitrile complex, we did obtain the same final product. The slight solubility of rhenium(V) chloride in nonpolar solvents is in agreement with that observed for $MoCl_5$[26] and precludes extensive investigation in this type of solvent. The reaction of triphenylphosphine and rhenium(V) chloride in benzene provides another example of the unique role of the solvent on the mode of reaction. The isolation of $[(C_6H_5)_3PH]_2Re_2Cl_9$ might result from the reaction of a small amount of water with rhenium(V) chloride to form the dinuclear species and the interaction of the liberated hydrogen chloride with the triphenylphosphine to form the cation. These results indicate that the hydrolysis scheme proposed by Allen, *et al.*,[9] is not limited to acetone. A cursory look at the reaction of rhenium(V) chloride with wet benzene shows the main product to be $ReOCl_3[P(C_6H_5)_3]_2$.

The main paths of the reaction of rhenium(V) chloride and triphenylphosphine in the various solvents are summarized in Figure 1.

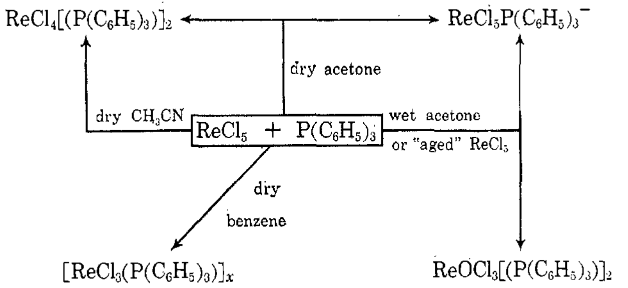

Figure 1.—Reactions of $ReCl_5$ and triphenylphosphine ($P(C_6H_5)_3$) under various conditions (major products only).

In the current work there is no evidence of a trinuclear cluster of rhenium(V). The use of a nonpolar solvent and a ligand with no reducing characteristics may lead to the isolation of such a species, but limited work with other systems in our laboratories has not indicated that such clusters are present. This phase of the investigation is still under way and the results will be reported later.

Acknowledgments.—G. E. wishes to express appreciation to the NSF for summer traineeships in 1967 and 1968.

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[22] F. Bonati and F. A. Cotton, *Inorg. Chem.*, **6**, 1353 (1967).

[23] G. B. Deacon, R. A. Jones, and P. E. Rogasch, *Aust. J. Chem.*, **16**, 360 (1963).

[24] H. G. Mayfield, Jr., and W. E. Bull, *Inorg. Chim. Acta*, **3**, 676 (1969).

[25] R. A. Bailey and F. J. Montillo, *J. Inorg. Nucl. Chem.*, **31**, 203 (1969).

[26] Bulletin Cdb-3A, Climax Molybdenum Co.