Oxidation–reduction titrations, method A, yield consumption ratios, $H_2O_2:VO^{2+}$, of 1.8–3.9 indicating that a chain reaction mechanism which involves net reaction 10 is present. Method B and O_2 evolution studies also suggest a chain mechanism. When initial conditions are controlled so that the reaction is speeded up (high peroxide, low acid), then the ratio H_2O_2 consumed: vanadyl consumed is lowered. When VO^{2+} is added slowly to H_2O_2 so that radical concentrations are low, H_2O_2 consumed is increased relative to vanadyl consumed.

Addition of VO_2^+ to the initial solution increases the O_2 evolution. Since increased $[VO_2^+]$ also increases the steady-state concentration of intermediate, the intermediate may be involved in a chain mechanism including reactions 11–13. For such a scheme, reaction 4 could also serve as a termination step.

$$I + H_2O_2 \longrightarrow O_2 + VO_2^+ + \cdot OH + H^+ \qquad (11)$$

$$I + \cdot OH \longrightarrow VO_2^+ + O_2 + H^+ \qquad (12)$$

$$2I \longrightarrow VO_3^+ + O_2 + VO^{3+} \qquad (13)$$

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The Redox Behavior of Rhenium Halides. II. The Reactivity of β-Rhenium(IV) Chloride in Nonaqueous Media

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The behavior of β-rhenium(IV) chloride in nonaqueous media has been studied to assess the variety of reactions this halide will undergo. Dissolution in acetonitrile is accompanied by some reduction, but *cis*-$ReCl_4 \cdot 2CH_3CN$ appears to be the principal reaction product. Studies on the systems β-$ReCl_4$–$(C_6H_5)_3P$–CH_3CN and β-$ReCl_4$–$(C_6H_5)_3P$–$(CH_3)_2CO$ reveal quite markedly different reaction products, the course of the reactions depending critically upon the reaction solvent. In the former, unreduced *trans*-$ReCl_4 \cdot 2(C_6H_5)_3P$ and reduced $[ReCl_3 \cdot (C_6H_5)_3P]_2$ and $ReCl_3 \cdot 2(C_6H_5)_3P \cdot CH_3CN$ are formed, whereas in acetone, oxygen abstraction occurs with the resulting formation of *trans*-$ReOCl_3 \cdot 2(C_6H_5)_3P$. The salt $(DOTP)_2Re_2Cl_9$ (DOTP = 1,1-dimethyl-3-oxobutyltriphenylphosphonium) is also isolated from the latter reaction. Direct reaction of β-rhenium(IV) chloride with anhydrous pyridine also leads to the formation of unreduced *cis*-$ReCl_4 \cdot 2C_5H_5N$ and reduced $(C_5H_5NH)_2Re_2Cl_8$ species.

Introduction

Since our original report of the existence of β-rhenium(IV) chloride,[1] subsequent papers have described details of its preparation[2-4] and structure.[5] An X-ray crystallographic study[5] revealed this halide to have a polymeric structure which contains dinuclear metal–metal bonded units of the $W_2Cl_9^{3-}$ type. However, although it resembles other tetrachlorides of the heavier transition metals of the early transition series (Nb, Ta, Mo, W) in exhibiting pronounced metal–metal bonding, its other structural features are quite different.[6-8]

Reactivity differences between these halides are also apparent. Thus MCl_4 (M = Nb, Ta, Mo, W) show a marked tendency to react with a variety of donor molecules (L) to form pseudooctahedral complexes of stoichiometry $MCl_4 \cdot 2L$.[9-12] On the other hand we found[1] that the reactions of β-$ReCl_4$, using acidified methanol or acetone as reaction solvents, afforded either rhenium(III) species derived from, or containing, the well-documented $Re_2Cl_8^{2-}$ anion[13] or oxorhenium(V) complexes. In no instances did we isolate rhenium(IV) complexes of the type $ReCl_4 \cdot 2L$. The apparent disproportionation of rhenium(IV) chloride into Re(III) and Re(V) appears to be quite general in solution *when the free access of air is permitted.*

When rigorously anhydrous and oxygen-free conditions are used, it has now been found that the reactions of β-rhenium(IV) chloride are sometimes quite different from those described above and rhenium(IV) complexes can indeed be isolated in certain instances.

Experimental Section

Materials.—Black crystalline β-rhenium(IV) chloride was obtained from the source described in an earlier paper.[1] All other reagents and solvents were commercially available and were used as supplied, except that solvents were dried by repeated distillation *in vacuo* from calcium hydride, phosphorus pentoxide, or anhydrous calcium sulfate.

Reaction Procedures.—To ensure the exclusion of oxygen and moisture, all reactions were carried out using an all-glass vacuum system using procedures described previously.[9,14] Once the reaction products had been isolated and dried, they could be handled in the atmosphere without fear of decomposition.

Reaction of β-Rhenium(IV) Chloride. (i) Acetonitrile.—

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We have previously reported[1] that β-rhenium(IV) chloride is insoluble in dry acetonitrile. However, if this halide is refluxed with this solvent for up to 72 hr under rigorously anhydrous conditions, it dissolves completely to give at first a dark yellow-brown solution which turns a dark green by the time solution is complete. Evaporation of this solution to dryness afforded a dark green solid. Analytical data showed that a pure product had not been isolated; analyses varied between samples from different runs. *Anal.* Found for three different reaction products: C, 12.93, 14.51, 13.72; H, 1.82, 2.18, 1.65; N, 7.83, 8.17, 8.02; Cl, 31.26; Re, 45.00.

These products were only very slightly soluble in chloroform, benzene, ether, ethanol, and dichloromethane but soluble in acetone and acetonitrile. Attempts to recrystallize these products by dilution of acetone solutions with cold water resulted in the precipitation of some black rhenium dioxide.

If the initial acetonitrile reaction mixtures were rapidly cooled to −196° after solution of the halide was complete, small amounts of a lighter green precipitate sometimes formed, which did not redissolve upon warming to room temperature. These materials could easily be isolated by filtration. Analysis showed that their composition approached that of $ReCl_4 \cdot 2CH_3CN$, although the chlorine analysis was rather low. *Anal.* Calcd for $ReCl_4 \cdot 2CH_3CN$: C, 11.71; H, 1.48; N, 6.83; Cl, 34.58. Found: C, 11.73; H, 1.73; N, 6.59; Cl, 32.44.

The infrared spectra of the soluble products (4000–400 cm^{-1}) showed, in addition to the usual absorption bands associated with coordinated acetonitrile,[15] several weak features which are assigned to vibrations of the $CH_3C(Cl){=}NH_2^+$ cation.[16] These vibrations are assigned as follows (cm^{-1}): $CH_3C(Cl){=}NH_2^+$ at ∼3220 (w, vbr) ($\nu(NH_2)$); 1693 (m–w), 1635 (w), and ∼1605 (w) ($\delta(NH_2)$); ∼1260 (w, sh) ($\rho(NH_2)$?); 690 (w) (ν(C–Cl)); CH_3CN at 2304 (w) (combination band);[15] 2280 (s) and 2240 (w) (ν(CN)); ∼1160 (w, br); 1020 (s) ($\rho(CH_3)$); 972 (w); 960 (w, sh); 950 (m–s); ∼915 (vw), ∼840 (w, sh), and ∼820 (w) (2δ(N–C–C)?); 420 and 406 (m–w) (δ(N–C–C)).

The soluble green products had reactions characteristic of rhenium(IV).

(a) The reaction of 0.091 g of a sample of the soluble product dissolved in 6 ml of methanol containing 2 ml of concentrated hydrochloric acid with an excess of tetraphenylarsonium chloride afforded 0.107 g of green crystalline $[(C_6H_5)_4As]_2ReCl_6$. *Anal.* Calcd for $[(C_6H_5)_4As]_2ReCl_6$: C, 49.43; H, 3.46. Found: C, 49.06; H, 3.52.

The diffuse-reflectance electronic absorption spectrum of this salt was characteristic of the $ReCl_6^{2-}$ anion,[17] with bands at 7300, 8700 and 9200 (doublet), and 14,300 cm^{-1} assigned to d ↔ d transitions.

(b) Treatment of a sample (0.094 g) of the dark green soluble product with an acetonitrile solution of triphenylphosphine gave *ca.* 0.03 g of red crystalline *trans*-$ReCl_4 \cdot 2(C_6H_5)_3P$[18] as the initial reaction product. *Anal.* Calcd for $ReCl_4 \cdot 2(C_6H_5)_3P$: C, 50.71; H, 3.55. Found: C, 51.00; H, 3.65.

(ii) **Triphenylphosphine. (a) Acetonitrile as Solvent.**—The reaction of β-rhenium(IV) chloride with triphenylphosphine (1:2 w/w) in refluxing anhydrous acetonitrile initially leads to the formation of mixed green, yellow, and red-brown solids and a yellow-brown solution. Reflux was continued until the insoluble material appeared to be homogeneously green. The reaction mixture was then filtered, the filtrate set aside, and the insoluble product washed (five times) with freshly distilled acetonitrile. The insoluble portion was extracted with hot dichloromethane until the washings, initially red, were colorless. The remaining insoluble green complex, $[ReCl_3 \cdot (C_6H_5)_3P]_2$, was finally washed with hot benzene and ether and dried *in vacuo*. *Anal.* Calcd for $[ReCl_3 \cdot (C_6H_5)_3P]_2$: C, 38.95; H, 2.72. Found: C, 38.90; H, 3.35.

The red dichloromethane washings from the extraction of the bulk insoluble reaction product were evaporated to dryness and the resulting red crystals of *trans*-$ReCl_4 \cdot 2(C_6H_5)_3P$ were washed thoroughly with hot acetone until the washings turned pink and then with ether to remove traces of an unidentified yellow contaminant. *Anal.* Calcd for $ReCl_4 \cdot 2(C_6H_5)_3P$: C, 50.71; H, 3.55; Cl, 16.63. Found: C, 50.49; H, 3.34; Cl, 16.61.

The original yellow reaction filtrate, which remained after separation of the bulk insoluble reaction product, was evaporated to dryness *in vacuo* and then washed with ethanol and then ether. When the ethanol washings were reduced in volume by evaporation, small quantities of mustard yellow $ReCl_3 \cdot 2(C_6H_5)_3P \cdot CH_3CN$ (identified by its infrared spectrum)[19] and glistening silvery gray plates of the ethoxy derivative $ReOCl_2(OC_2H_5) \cdot 2(C_6H_5)_3P$ deposited. *Anal.* Calcd for $ReOCl_2(OC_2H_5) \cdot 2(C_6H_5)_3P$: C, 53.60; H, 4.19. Found: C, 54.50; H, 4.35.

The remaining green insoluble product was dissolved in dichloromethane, the solution was filtered, and an equal volume of ethanol was added. The filtrate was immediately evaporated to low volume, whereupon a green precipitate formed. This was filtered off and discarded, and the procedure was repeated until evaporation afforded a mustard-colored precipitate. The latter was washed with ethanol and ether and then dried. It was recrystallized as orange plates from acetone–acetonitrile. *Anal.* Calcd for $ReCl_3 \cdot 2(C_6H_5)_3P \cdot CH_3CN$: C, 52.64; H, 3.88; N, 1.63. Found: C, 50.96; H, 3.84; N, 1.71.

This complex had infrared (4000–200 cm^{-1}) and electronic absorption spectra identical with those of a sample prepared by the method of Rouschias and Wilkinson[19] from *trans*-$ReOCl_3 \cdot 2(C_6H_5)_3P$ and acetonitrile.

(b) **Acetone as Solvent.**—Reaction between β-rhenium(IV) chloride and excess triphenylphosphine in anhydrous acetone was rapid and a green product began to form immediately after the reagents were mixed. After 3 hr of reaction (with shaking), the yellow-green insoluble product was filtered from the purple solution and washed with acetone until the washings were no longer colored and then with ether. It was recrystallized from benzene–petroleum ether (bp 30–60°) to give yellow crystals of *trans*-$ReOCl_3 \cdot 2(C_6H_5)_3P$. *Anal.* Calcd for $ReOCl_3 \cdot 2(C_6H_5)_3P$: C, 52.00; H, 3.61. Found: C, 51.17; H, 3.88.

The purple acetone reaction filtrate was evaporated to dryness and washed with ethanol, then acetone, and finally ether before being dried *in vacuo*. Its infrared spectrum very closely resembled that of the 1,1-dimethyl-3-oxobutyltriphenylphosphonium cation[20] and the low-frequency infrared spectrum (450–200 cm^{-1}) and electronic absorption spectrum showed the presence of the dinuclear $Re_2Cl_9^{2-}$ anion.[1,21] On the basis of the foregoing evidence and the analytical data, this product is formulated as the acetone solvate $[CH_3COCH_2C(CH_3)_2P(C_6H_5)_3]_2Re_2Cl_9 \cdot 2(CH_3)_2CO$. *Anal.* Calcd for $[C_{24}H_{26}OP]_2Re_2Cl_9 \cdot 2(CH_3)_2CO$: C, 42.36; H, 4.22; P, 4.05; Cl, 20.85. Found: C, 43.14; H, 3.89; P, 3.86; Cl, 19.82.

(iii) **Pyridine.**—The halide dissolved slowly in anhydrous pyridine to give a violet solution which had turned a dark brown after 20 hr of reaction. The solution was filtered and evaporated to dryness. The resulting solid was extracted with hot chloroform until the washings were colorless and the latter set aside. The green insoluble residue was finally washed with hot acetone and the washings once again were saved. Analysis showed the green material to be impure $(C_5H_5NH)_2Re_2Cl_8$. *Anal.* Calcd for $(C_5H_5NH)_2Re_2Cl_8$: C, 14.66; H, 1.50; N, 3.70. Found: C, 16.56; H, 1.64; N, 3.55.

This product had infrared and diffuse-reflectance electronic spectra identical with those of an authentic sample of this salt.[18]

The acetone washings from the above work-up were taken to dryness, and the brown solid remaining, after being washed with ethanol and ether, was dried *in vacuo*. *Anal.* Calcd for $ReCl_4 \cdot 2C_5H_5N$: C, 24.69; H, 2.07; N, 5.76; Cl, 29.17. Found: C, 24.26; H, 2.29; N, 5.40; Cl, 30.14.

This complex had an infrared spectrum characteristic of coordinated pyridine and a diffuse-reflectance spectrum which confirmed it to be a derivative of rhenium(IV). This same complex was isolated by a similar work-up of the chloroform washings from the extraction of the bulk reaction product. Its low-frequency infrared spectrum (400–200 cm^{-1}) showed ν(Re–Cl) modes located at 344(m–s), 319 (s), and 307 (sh) cm^{-1} consistent with a *cis*-$MX_4 \cdot 2L$ stereochemistry.

(iv) **Triphenylarsine.**—When acetonitrile was used as the solvent, a green solution and green solid resulted. After a reaction time of 24 hr the reaction mixture was filtered and the insoluble product was washed with acetonitrile and dried *in vacuo*. *Anal.* Calcd for $[ReCl_3 \cdot (C_6H_5)_3As]_2$: C, 36.11; H, 2.53. Found: C, 35.11; H, 2.44.

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(15) See, for example, R. A. Walton, *Spectrochim. Acta*, **21**, 1795 (1965).

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Its low-frequency infrared spectrum (450–200 cm^{-1}) was very similar to that of $[ReCl_3 \cdot (C_6H_5)_3P]_2$, implying a close structural relationship between these two complexes: 395 (vw), 355 (sh), and 351 (s) (ν(Re–Cl)); 340 (sh) and 315 (s) (ν(Re–Cl)) for $[ReCl_3 \cdot (C_6H_5)_3As]_2$; 448 (m), 416 (m), 394 (w), 349 (s) (ν(Re–Cl)), ~328 (w, br, sh), and 310 (m–s) (ν(Re–Cl)) for $[ReCl_3 \cdot (C_6H_5)_3P]_2$.

The reaction filtrate upon evaporation left a green residue which was washed well with warm dichloromethane and ether. *Anal.* Calcd for $ReCl_4 \cdot 2CH_3CN$: C, 11.71; H, 1.48; N, 6.83; Cl, 34.58. Found: C, 11.74; H, 1.23; N, 6.14; Cl, 32.65.

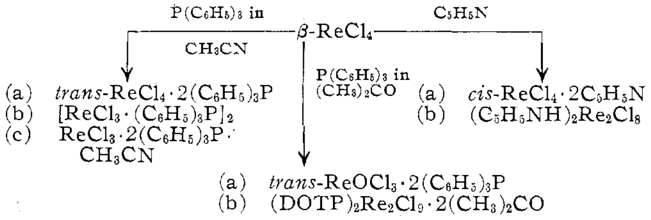
The infrared spectrum of this product was identical with that of the green insoluble product isolated from the $ReCl_4$–CH_3CN reaction and believed to be $ReCl_4 \cdot 2CH_3CN$. Its low-frequency infrared spectrum (ν(Re–Cl) at 363 (m–s), 328 (s) (doublet?), 295 (sh), and 280 (m–w) cm^{-1}) resembles that of *cis*-$ReCl_4 \cdot 2C_5H_5N$ and a related cis stereochemistry seems likely.

(v) **Thiourea.**—Using *anhydrous* acetone as solvent, the insoluble red complex $ReCl_3 \cdot 3(NH_2)_2CS \cdot {}^1/_3(CH_3)_2CO$[1] was the principal reaction product.

Physical Measurements.—Infrared spectra were recorded as Nujol mulls using KBr plates (4000–400 cm^{-1}) and polythene sheets (400–200 cm^{-1}) on Perkin-Elmer Model 237, Beckman IR-10 or IR-11, and Grubb-Parsons DM 4 spectrophotometers. Diffuse-reflectance spectra were measured on a Unicam SP-700 spectrophotometer and solution electronic spectra on a Unicam SP-800 spectrophotometer. The magnetic susceptibility of the $ReCl_4$–CH_3CN reaction product was determined using a Gouy-balance system and for $ReCl_3 \cdot (NH_2)CS \cdot {}^1/_3(CH_3)_2CO$ a Faraday balance was used.[22]

Results and Discussion

We find from the present study that when anhydrous oxygen-free conditions are used, the reactions of β-rhenium(IV) chloride are even more varied than was previously noted.[1] Thus its reactions with triphenylphosphine in *anhydrous* acetone or acetonitrile and with *anhydrous* pyridine are as outlined in the following reaction sequences (DOTP = 1,1-dimethyl-3-oxobutyltriphenylphosphonium).[20] In all instances, the reaction products were characterized on the basis of their infrared and electronic absorption spectral properties.



Our initial studies involved the reaction of β-rhenium(IV) chloride with triphenylphosphine in refluxing acetonitrile. The insoluble reaction product was a mixture of *trans*-$ReCl_4 \cdot 2(C_6H_5)_3P$ and the metal–metal bonded dimer $[ReCl_3 \cdot (C_6H_5)_4P]_2$[1] which could easily be separated since the rhenium(IV) complex is soluble in dichloromethane. From the reaction filtrate small quantities of $ReCl_3 \cdot 2(C_6H_5)_3P \cdot CH_3CN$ were isolated. Clearly, dissolution of the halide in acetonitrile does not result in the immediate and quantitative reduction to rhenium(III), since *trans*-$ReCl_4 \cdot 2(C_6H_5)_3P$ can be isolated. However, under the reflux conditions we used, some reduction obviously occurs. This is accompanied by the evolution of hydrogen chloride, and under these acidic conditions the $Re_2Cl_8^{2-}$ species which is presumably first formed evidently reacts with triphenylphosphine in the usual fashion[1] to yield $[ReCl_3 \cdot (C_6H_5)_3P]_2$.

Paralleling the above observations we find that in its reaction with anhydrous pyridine, β-rhenium(IV) chloride affords both unreduced *cis*-$ReCl_4 \cdot 2C_5H_5N$ and reduced $(C_5H_5NH)_2Re_2Cl_8$. This reaction should be contrasted with that we had previously observed in acetone,[1] from which we isolated $Re_2O_3(C_5H_5N)_4Cl_4$, $[ReO_2(C_5H_5N)_4]Cl \cdot 2H_2O$, and $(C_5H_5NH)_2Re_2Cl_8$ but no derivatives of rhenium(IV). Clearly in the present reaction, anhydrous pyridine acts as both the reducing agent and Lewis base.

In contrast to the above conclusions, we were initially uncertain as to whether acetonitrile or triphenylphosphine was the reducing agent in the β-$ReCl_4$–$(C_6H_5)_3P$–CH_3CN system, although acetonitrile was suspected in view of its tendency to reduce halides such as $MoCl_5$,[23] WCl_5,[23] and $ReCl_5$.[24] Accordingly, the chloride was allowed to react directly with acetonitrile to afford a dark green solution after reflux for 72 hr. Evaporation of this solution to dryness gave a dark green solid, but elemental analysis indicated it was not a pure phase. Indeed the infrared spectrum of this product showed the presence of the $CH_3C(Cl){=}NH_2^+$ cation, in addition to coordinated acetonitrile (Experimental Section). Since this cation is formed by the reaction of acetonitrile with HX (X = Cl, Br),[25] it seems likely that it is formed during the partial reduction of β-rhenium(IV) chloride by acetonitrile.[26] However, that reduction had not proceeded to any great extent was suggested from a magnetic moment determination. Assuming that the average composition of the green soluble product approached $ReCl_{3.7}(CH_3CN)_{2.4}$ (see Experimental Section), then $\mu_{eff} = 3.0\ (\pm 0.1)$ BM at 293°K, somewhat lower than the value for $ReCl_4 \cdot 2CH_3CN$ reported by Rouschias and Wilkinson (3.40 BM at 293°K)[24] but much greater than that expected for magnetically dilute rhenium(III) species[28] or diamagnetic metal–metal bonded $Re_2Cl_6L_2$. That this product contained $ReCl_4 \cdot 2CH_3CN$ was suggested by the following observations. (i) Reaction with triphenylphosphine in acetonitrile afforded red crystalline *trans*-$ReCl_4 \cdot 2(C_6H_5)_3P$, and with tetraphenylarsonium chloride in CH_3OH–HCl, $[(C_6H_5)_4As]_2ReCl_6$ could be isolated. Both of these reactions are characteristic of $ReCl_4 \cdot 2CH_3CN$.[24] (ii) The diffuse-reflectance spectra of the soluble and insoluble products from the β-$ReCl_4$–CH_3CN reaction (see Experimental Section), were characteristic of octahedral rhenium(IV) species (Figure 1), with absorption bands in the region 5000–9000 cm^{-1} and ~13,000 cm^{-1}.

Since the soluble product from this reaction does not afford any $[ReCl_3 \cdot (C_6H_5)_3P]_2$ when treated with triphenylphosphine (see (i) above), it is reasonable to assume that dinuclear Re–Re bonded species are *not* formed in significant amounts when β-rhenium(IV)

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[22] This latter measurement was carried out by Dr. R. Whyman at ICI, Runcorn, Cheshire, England.

[23] E. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *J. Chem. Soc.*, 4531 (1964).

[24] G. Rouschias and G. Wilkinson, *ibid.*, *A*, 489 (1968).

[25] (a) S. W. Peterson and J. M. Williams, *J. Amer. Chem. Soc.*, **88**, 2866 (1966); (b) J. M. Williams, S. W. Peterson, and G. M. Brown, *Inorg. Chem.*, **7**, 2577 (1968).

[26] The reduction of metal chlorides by acetonitrile is known to proceed with the evolution of hydrogen chloride. Recently, a detailed study of the reduction of vanadium(IV) chloride has shown that the main organic oxidation product is 2-methyl-4,6-bis(trichloromethyl)-1,3,4-triazine.[27] We find no evidence for the presence of significant amounts of the latter compound in our reaction products.

[27] C. A. A. Van Driel and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, **88**, 891 (1969).

[28] See, for example, B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 152 (1964).

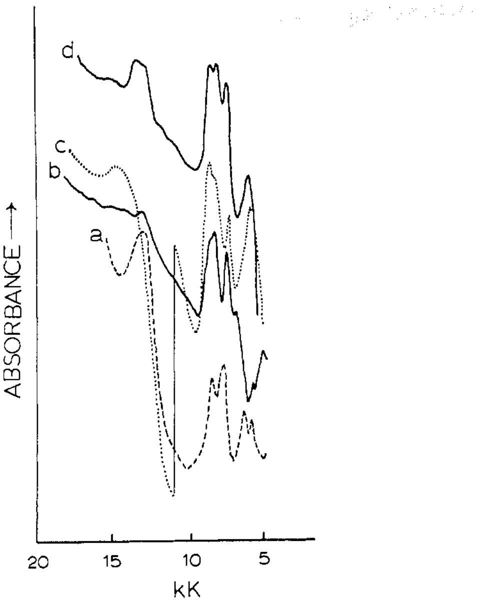

Figure 1.—Diffuse reflectance spectra of rhenium(IV) complexes: (a) *trans*-$ReCl_4 \cdot 2(C_6H_5)_3P$; (b) *cis*-$ReCl_4 \cdot 2C_5H_5N$; (c) soluble product from the β-$ReCl_4$–CH_3CN system; (d) insoluble product from the β-$ReCl_4$–CH_3CN system.

chloride dissolves in acetonitrile, in the *absence* of triphenylphosphine. Under these conditions it seems likely that $ReCl_4 \cdot 2CH_3CN$ is the principal reaction product although there is obviously contamination by some reduction product. However, when triphenylphosphine is present, the reduction is apparently enhanced, and the acidic conditions prevailing in solution from the evolution of hydrogen chloride then favor the formation of $[ReCl_3 \cdot (C_6H_5)_3P]_2$.

The isolation of small amounts of $ReCl_3 \cdot 2(C_6H_5)_3P \cdot CH_3CN$ from the filtrate of the β-$ReCl_4$–$(C_6H_5)_3P$–CH_3CN system probably results from the reaction of *trans*-$ReCl_4 \cdot 2(C_6H_5)_3P$ with acetonitrile, since Rouschias and Wilkinson[24] have observed that $ReCl_3 \cdot 2(C_6H_5)_3P \cdot CH_3CN$ is formed upon prolonged heating of these two reactants.[29,30]

A study of the β-$ReCl_4$–$(C_6H_5)_3As$–CH_3CN system indicates an essentially analogous reaction course to that described above for the related triphenylphosphine reaction. However, in contrast, $ReCl_4 \cdot 2(C_6H_5)_3As$ is not formed, but instead $ReCl_4 \cdot 2CH_3CN$ is isolated as the unreduced rhenium species. This latter observation is not unexpected since the formation of $ReCl_4 \cdot 2(C_6H_5)_3As$ from the reaction of $ReCl_4 \cdot 2CH_3CN$ and triphenylarsine has been found to proceed only when the acetonitrile which is liberated can escape.[24] Under our reaction conditions, the reaction was carried out in an excess of acetonitrile in a closed system.

The formation of $ReOCl_3 \cdot 2(C_6H_5)_3P$ from the reaction of β-rhenium(IV) chloride with triphenylphosphine in *anhydrous* acetone must involve oxygen abstraction from the solvent, a not uncommon feature of the chemistry of higher oxidation state halides of the transition metals of groups IV–VII.[8] However, oxygen abstraction does not always accompany the reaction of this halide in acetone, since under similar reaction conditions to those used to prepare $ReOCl_3 \cdot 2(C_6H_5)_3P$, thiourea reacts to form the unusual rhenium(III) complex $ReCl_3 \cdot 3(NH_2)_2CS \cdot {}^1/_3(CH_3)_2CO$[1] ($\mu_{eff}$ = 1.55 BM at 293°K).

From the filtrate of the reaction between β-rhenium(IV) chloride and triphenylphosphine in acetone, a purple solid could be isolated, the infrared spectrum of which was virtually identical with that recently reported by Gehrke, *et al.*,[20] for the complex $[CH_3COCH_2C(CH_3)_2P(C_6H_5)_3]_2ReCl_6$ (abbreviated $(DOTP)_2ReCl_6$)[20] which is formed by the reaction of $ReOCl_3 \cdot 2(C_6H_5)_3P$ with hydrogen chloride in acetone. Thus the oxygen-abstraction reaction which leads to the formation of $ReOCl_3 \cdot 2(C_6H_5)_3P$ is presumably accompanied by the liberation of hydrogen chloride thereby generating reaction conditions favorable for the formation of the DOTP cation. The purple color of this product is characteristic of the $Re_2Cl_9^{2-}$ anion,[1,21] and the presence of the latter species was confirmed from spectral measurements. First, its low-frequency infrared spectrum showed ν(Re–Cl) vibrations at 333 (s) and 300 (m–w) cm^{-1}, very close in frequency to the related modes in $[(C_6H_5)_4As]_2Re_2Cl_9$[1] (327 (s) and 297 (m–w) cm^{-1}). Second, its diffuse-reflectance spectrum resembles that of $[(C_6H_5)_4As]_2Re_2Cl_9$,[1] with absorption bands at 14,000, ~17,800, 27,800, 31,000, 35,900, and 36,800 (doublet) cm^{-1}, characteristic of the $Re_2Cl_9^{2-}$ anion.[1,21] An acetonitrile solution of this complex showed its two lowest energy electronic absorption bands at 14,800 (ε 2150) and 18,380 (ε ~300), implying that the anion was not *immediately* disrupted upon dissolution in this solvent. A conductance measurement on this same solution ($C_m = 1.3 \times 10^{-3}$ mol $l.^{-1}$) showed that Λ_m = 197 ohm^{-1} cm^2, consistent with its anticipated 2:1 electrolyte behavior. Finally the analytical data indicate that two molecules of acetone are also associated with this complex, but we have no further direct evidence for this since the very intense infrared ν(C–O) cation absorption at 1715 cm^{-1} is likely to obscure the corresponding vibration of acetone. However, a shoulder on the low-energy side of the 1715-cm^{-1} band (at ~1700 cm^{-1}) may arise from ν(C–O) of these acetone molecules.

Since the completion of our study, Gehrke and Eastland[31] have reported the reaction of rhenium(V) chloride with triphenylphosphine in a variety of solvents, including acetone. From their results it is apparent that in this latter solvent a complex series of reactions occurs, not unrelated to those we have observed with β-rhenium(IV) chloride. Among the products they isolated were $ReOCl_3 \cdot 2(C_6H_5)_3P$ and $(DOTP)_2Re_2Cl_9$, although the latter complex was not isolated in a pure state by this route. Thus both β-rhenium(IV) chloride and rhenium(V) chloride very readily undergo oxygen-abstraction and reduction reactions, the latter often leading to dinuclear metal–metal bonded species.

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(29) The structure of $ReCl_3 \cdot 2(C_6H_5)_3P \cdot CH_3CN$ has recently been established from a single-crystal X-ray analysis.[30] This octahedral complex contains N-bonded acetonitrile and has trans rhenium–phosphorus bonds.

(30) M. G. B. Drew, D. G. Tisley, and R. A. Walton, *Chem. Commun.*, 600 (1970).

(31) H. Gehrke, Jr., and G. Eastland, *Inorg. Chem.*, **9**, 2722 (1970).