Mixed Chloride/Phosphine Complexes of the Dirhenium Core. 5. Reduction or Disproportionation at the Re_2^{6+} Unit in Reactions with Tertiary Phosphines in Different Solvents

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For reactions of the octachlorodirhenium anion, $[Re_2Cl_8]^{2-}$, with tertiary phosphines PEt_3 and PPr^n_3, the influence of solvent on the reaction pathway has been studied. It has been shown that in 1-propanol at room temperature the reaction leads to a one-electron reduction of the Re_2^{6+} core. The novel dirhenium(II,III) paramagnetic products of stoichiometries $[Bu^n_4N][Re_2Cl_6(PEt_3)_2]$ (**1a**) and $Re_2Cl_5(PPr^n_3)_3$ (**2a**) have been isolated and characterized. In benzene a disproportionation process occurs resulting in mononuclear rhenium(IV) complexes $ReCl_4(PR_3)_2$ (PR_3 = PEt_3 (**1b**) and PPr^n_3 (**2b**)) in addition to **1a** and **2a**, respectively. The solid state structures of compounds **1a**, **1b**, **2a**$\cdot 0.25C_6H_{14}$, and **2b** have been investigated by X-ray crystallography. The crystallographic parameters are as follows: for **1a**, tetragonal space group $P4_2/m$ with $a = 11.821(2)$ Å, $c = 14.770(3)$ Å, and $Z = 2$; for **1b**, monoclinic space group $P2_1/n$ with $a = 8.0555(4)$ Å, $b = 12.536(2)$ Å, $c = 10.2041(6)$ Å, $\beta = 99.167(9)°$, and $Z = 2$; for **2a**$\cdot 0.25C_6H_{14}$, monoclinic space group $P2_1/n$ with $a = 11.7679(9)$ Å, $b = 18.574(5)$ Å, $c = 19.688(4)$ Å, $\beta = 93.37(2)°$, and $Z = 4$; for **2b**, monoclinic space group $P2_1/c$ with $a = 8.219(2)$ Å, $b = 11.210(1)$ Å, $c = 14.331(3)$ Å, $\beta = 93.171(9)°$, and $Z = 2$. It has also been found that the disproportionation process in benzene goes by way of an intermediate complex which is an initial product of interaction between the $[Re_2Cl_8]^{2-}$ and the phosphine. In the case of the triethylphosphine ligand we formulate this complex as $[Bu^n_4N][Re_2Cl_7(PEt_3)_3]$ (**1c**).

Introduction

The reactions of $[Re_2Cl_8]^{2-}$ have been both important and poorly understood since first reported by Walton.[1] Alcohols have long been used as reaction media for one- and two-electron reduction of octachlorodirhenate anions with phosphines under reflux conditions giving the products $Re_2Cl_5(PR_3)_3$ (PR_3 = $PMePh_2$, $PEtPh_2$)[1] and $Re_2Cl_4(PR_3)_4$ (PR_3 = PMe_3, PEt_3, PPr^n_3, PMe_2Ph, PEt_2Ph).[1−3] It has more recently been reported that a one-electron reduction of $[Re_2Cl_8]^{2-}$ occurs in alcohols instantly at room temperature when it reacts with the most basic phosphines such as PMe_3[4] and PMe_2Ph[5] producing the 1,2,7-isomers of $Re_2Cl_5(PR_3)_3$. The reduced rhenium species have also been found in other media, such as acetone,[1,2] benzene,[5,6] and acetonitrile.[5] However, the process has been shown[5−7] to be very dependent on the solvent used in terms of rates, intermediates, and the final products. At this point we are almost sure that phosphines themselves cannot serve as reducing agents (at least, at moderate temperatures) for the reduction of the dirhenium(III) complexes. In the present work we have studied the reactions of $[Re_2Cl_8]^{2-}$ with PEt_3 and PPr^n_3 in two different solvents, one of which, propanol, can be oxidized, whereas the reducing ability of the other one, benzene, must be negligible.

Several important findings have been made as a result of this study, namely: (1) in propanol, both PEt_3 and PPr^n_3 cause a one-electron reduction of the $[Re_2Cl_8]^{2-}$ under mild reaction conditions; (2) the reduced products, which have the Re_2^{5+} core, are different, $[Re_2Cl_6(PEt_3)_2]^-$ and $Re_2Cl_5(PPr^n_3)_3$, respectively; (3) in benzene, there is a disproportionation process, $3Re_2^{6+} \rightarrow 2Re_2^{5+} + 2Re^{4+}$, rather than reduction; and (4) there is an intermediate complex in solution as an initial product of interaction between the $[Re_2Cl_8]^{2-}$ and phosphine in benzene, which further undergoes the disproportionation.

Experimental Section

General Procedures. All of the syntheses and purifications were carried out under an atmosphere of N_2 in standard Schlenkware. All solvents were freshly distilled under N_2 from suitable drying agents. Chemicals were purchased from the following commercial sources and used as received: PEt_3 and PPr^n_3, Strem Chemicals; $[Bu^n_4N]_2[Re_2Cl_8]$, Aldrich, Inc.

Physical Measurements. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. A stream of nitrogen was bubbled through the solution during the measurements. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the Ag/AgCl electrode at room temperature. Under our experimental conditions, $E_{1/2} = +0.47$ V vs Ag/AgCl for the ferrocenium/ferrocene couple. Voltammetric experiments were carried out with the use of Bioanalytical Systems Inc. electrochemical analyzer, Model 100. The scan rate was 100 mV/s at a Pt disk electrode. Elemental analyses were carried out by Canadian Microanalytical Services, Ltd. X-band ESR spectra of dichloromethane glasses were recorded at 100 K with a frequency of 9.4 GHz on a Bruker ESR 300 spectrometer.

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The positive and negative FAB/DIP mass spectra were acquired using a VG Analytical 70S high-resolution, double-focusing, sectored (EB) mass spectrometer. Samples for analyses were prepared by mixing a solution of each compound in CH_2Cl_2 or $CHCl_3$ with an NBA matrix on the direct insertion probe tip.

Synthetic Procedures. (A1) Reaction of $[Bu^n_4N]_2[Re_2Cl_8]$ with PEt_3 in 1-Propanol To Give 1a. To a suspension containing $[Bu^n_4N]_2[Re_2Cl_8]$ (0.277 g, 0.24 mmol) in 15 mL of 1-propanol was added 1 mL of triethylphosphine. Within 30 min at room temperature the color of the solid turned to grass-green. This solid was shown to be the dirhenium(III) complex $Re_2Cl_6(PEt_3)_2$.[8] As the stirring continued, the precipitate was gradually dissolving, giving a dark-green solution. Even after 1 week of stirring an appreciable amount of solid was still present (about 25% based on the total amount of Re). The resulting solution was filtered and evaporated to dryness, affording a green residue. It was then washed with hexanes (2 × 10 mL), dried, and dissolved in 8 mL of acetone. The acetone solution was layered with 15 mL of isomeric hexanes. The large green crystals of $[Bu^n_4N][Re_2Cl_6(PEt_3)_2]$ (**1a**) appeared at room temperature in a few days. Yield: 0.168 g (65%).

Anal. Calcd for $Re_2P_2NCl_6C_{28}H_{66}$ (**1a**): Cl, 19.99; N, 1.32; C, 31.61; H, 6.25. Found: Cl, 19.94; N, 1.29; C, 31.73; H, 6.02.

For $[Re_2Cl_6(PEt_3)_2]^-$, CV (CH_2Cl_2, 22 °C, V vs Ag/AgCl): $E_{1/2}(\text{ox}) = -0.08$, $E_{p,a} = -1.17$.

−FAB/DIP-MS (NBA/$CHCl_3$, *m/z*): 822 ($[M]^-$), 785 ($[M - Cl]^-$), 704 ($[M - PEt_3]^-$), 673 ($[M - PEt_3 - Cl]^-$), 584 ($[M - 2PEt_3]^-$), 551 ($[M - 2PEt_3 - Cl]^-$). ESR (CH_2Cl_2, 100 K) centered at 2698 G, $g = 2.49$.

(A2) Reaction of $[Bu^n_4N]_2[Re_2Cl_8]$ with PEt_3 in Benzene To Give 1a and 1b. $[Bu^n_4N]_2[Re_2Cl_8]$ (0.336 g, 0.29 mmol) was placed in 20 mL of benzene, and 1 mL of PEt_3 was added to the suspension. The mixture was stirred at 60 °C without reflux for 3 h yielding a red-brown solution. After it was cooled to room temperature, all volatile components were removed under vacuum to give a brown residue, which was washed with 20 mL of hexanes, dried, and then dissolved in 8 mL of acetone. The hexane washings were kept. The resulting brown solution was layered with 15 mL of hexanes. Green block-shaped crystals of **1a** appeared in a day at room temperature. Yield: 0.199 g (64%).

The orange-red hexane washings were reduced in volume by half at low pressure and cooled to about 0 °C for several days to afford red crystals of the mononuclear complex $ReCl_4(PEt_3)_2$ (**1b**). Yield: 0.033 g (20% based on amount of Re).

Anal. Calcd for $ReP_2Cl_4C_{12}H_{30}$ (**1b**): C, 25.53; H, 5.37. Found: C, 25.81; H, 5.43. CV (CH_2Cl_2, 22 °C, V vs Ag/AgCl): $E_{1/2}(\text{red}) = -0.33$. +FAB/DIP-MS (NBA/$CHCl_3$, *m/z*): 528 ($[M - Cl]^+$), 491 ($[M - 2Cl]^+$), 410 ($[M - PEt_3 - Cl]^+$), 327 ($[M - 2PEt_3]^+$).

(B1) Reaction of $[Bu^n_4N]_2[Re_2Cl_8]$ with PPr^n_3 in 1-Propanol To Give 2a. To a suspension containing $[Bu^n_4N]_2[Re_2Cl_8]$ (0.321 g, 0.28 mmol) in 15 mL of 1-propanol was added 1 mL of tri-*n*-propylphosphine. The mixture was stirred at room temperature for 15 h, giving a green-brown solution. All volatiles were removed to leave a green-brown residue, which was dried overnight and then extracted with 25 mL of warm hexanes. The extract was filtered, and its volume was reduced at low pressure to 8 mL. Green crystals of $Re_2Cl_5(PPr^n_3)_3$ (**2a**) were obtained after a saturated solution was kept at 0 °C for a few days. Yield: 0.205 g (71%).

Anal. Calcd for $Re_2P_3Cl_5C_{27}H_{63}$ (**2a**): C, 31.47; H, 6.18. Found: C, 31.59; H, 6.11. CV (CH_2Cl_2, 22 °C, V vs Ag/AgCl): $E_{1/2}(\text{red}) = -0.90$, $E_{1/2}(\text{ox}) = +0.34$. +FAB/DIP-MS (NBA/$CH_2Cl_2$, *m/z*): 1029 ($[M]^+$), 994 ($[M - Cl]^+$), 869 ($[M - PPr_3]^+$), 834 ($[M - PPr_3 - Cl]^+$), 711 ($[M - 2PPr_3]^+$), 672 ($[M - 2PPr_3 - Cl]^+$), 551 ($[M - 3PPr_3]^+$). ESR ($CH_2Cl_2$, 100 K) centered at 2677 G, $g = 2.51$.

(B2) Reaction of $[Bu^n_4N]_2[Re_2Cl_8]$ with PPr^n_3 in Benzene To Give 2a and 2b. To a suspension of $[Bu^n_4N]_2[Re_2Cl_8]$ (0.183 g, 0.16 mmol) in 15 mL of benzene was added 1 mL of PPr^n_3. The mixture was stirred for 3 h at 60 °C, resulting in a red-brown solution. All volatile components were removed from the solution to give a red-brown residue, which was extracted with 20 mL of warm hexanes. The red solution was then filtered, and the filtrate was cooled to 0 °C, affording in 1 day a mixture of green and red crystals in an approximate ratio 2:1. The crystals were separated manually and were identified as **2a**·$0.25C_6H_{14}$ and the mononuclear complex $ReCl_4(PPr^n_3)_2$ (**2b**), respectively. The overall yield (based on total Re) was 86%.

Anal. Calcd for $ReP_2Cl_4C_{18}H_{42}$ (**2b**): C, 33.34; H, 6.54. Found: C, 33.18; H, 6.49. CV (CH_2Cl_2, 22 °C, V vs Ag/AgCl): $E_{1/2}(\text{red}) = -0.35$.

X-ray Crystallographic Procedures. Single crystals of compounds **1a**, **1b**, **2a**·$0.25C_6H_{14}$, and **2b** were obtained as described above. The X-ray diffraction study for **2b** was performed with an Enraf-Nonius CAD-4S diffractometer and graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) by using methods described previously.[9a,b] A suitable single crystal was affixed to the end of a quartz fiber with grease in a cold nitrogen stream (−120 °C). No appreciable decay was observed, as judged by periodic monitoring of the intensities of three standard reflections. The intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction based on a series of ψ scans was also applied.

X-ray diffraction experiments for **1a**, **1b**, and **2a**·$0.25C_6H_{14}$ were carried out on a Nonius FAST diffractometer with an area detector using Mo Kα radiation. Details for data collection have been fully described elsewhere.[9c] Each crystal was mounted on the tip of a quartz fiber with silicone grease, and the setup was quickly placed in the cold N_2 stream (−60 °C) of a Model FR 558-S low-temperature controller. Fifty reflections were used in cell indexing and about 240 reflections in cell refinement. Axial images were used to confirm the Laue group and all dimensions. The data were corrected for Lorentz and polarization effects by the MADNES program.[10] Reflection profiles were fitted and values of F^2 and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR.[11] The intensities for **2a**·$0.25C_6H_{14}$ were corrected for absorption using a local adaptation of the program SORTAV.[12]

All calculations were carried out on a DEC Alpha running VMS. The structures were solved and refined using the SHELXTL direct methods[13] and the SHELXL-93 programs.[14] All hydrogen atoms for molecule **1b** were refined independently. The H atoms for **2a**·$0.25C_6H_{14}$ and **2b** were included in the structure factor calculations at idealized positions.

All crystals of **1a** obtained by various techniques were twinned, and reflections were extremely broad. We were not able to completely model the disorder problem for ethyl groups in PEt_3 ligands and butyl groups in the $[Bu^n_4N]^+$ cation. Although there is no doubt concerning the core structure of molecule **1a**, the refinement was poor ($R = 0.106$), and we regard this result as a confirmation of the nature of the reaction product only. In the structure of **2a**·$0.25C_6H_{14}$ three perpendicular orientations of the Re_2 unit in the P_3Cl_5 cube of ligands were located, all leading to the same isomer. Their site occupancy factors (sof) were refined and converged to final values of 0.901, 0.051, and 0.048.

Relevant crystallographic data for complexes **1b**, **2a**·$0.25C_6H_{14}$, and **2b** are summarized in Table 1. X-ray experiments were also carried out for the complex **2a**[15] without molecules of crystallization solvent

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Table 1. Crystallographic Data for *trans*-$ReCl_4(PEt_3)_2$ (**1b**), 1,3,6-$Re_2Cl_5(PPr^n_3)_3$·$0.25C_6H_{14}$ (**2a**·$0.25C_6H_{14}$), and *trans*-$ReCl_4(PPr^n_3)_2$ (**2b**)

	1b	**2a**·$0.25C_6H_{14}$	**2b**
formula	$ReCl_4P_2C_{12}H_{30}$	$Re_2Cl_5P_3C_{28.5}H_{66.5}$	$ReCl_4P_2C_{18}H_{42}$
fw	564.30	1051.88	648.46
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	8.0555(4)	11.7679(9)	8.219(2)
b, Å	12.536(2)	18.574(5)	11.210(1)
c, Å	10.2041(6)	19.688(4)	14.331(3)
β, deg	99.167(9)	93.37(2)	93.171(9)
V, Å^3	1017.3(2)	4296(2)	1318.4(4)
Z	2	4	2
ρ_{calcd}, g·cm^{-3}	1.842	1.626	1.634
μ, mm^{-1}	6.643	6.070	5.137
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, °C	−60	−60	−120
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0294, 0.0790	0.0455, 0.1048	0.0249, 0.0650
R1,[a] wR2[b] (all data)	0.0330, 0.0840	0.0545, 0.1123	0.0413, 0.0702

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

and another polymorph of **1b**.[16] These data can be found in the Supporting Information.

Results and Discussion

Syntheses. Reactions of $[Re_2Cl_8]^{2-}$ with PEt_3 and PPr^n_3 in 1-propanol lead exclusively to the one-electron reduction of the dirhenium(III,III) complex and to the formation of Re_2^{5+} products. To this extent, the two phosphines studied in this work behave in the same manner as the basic but sterically less demanding phosphine ligands, PMe_3 and PMe_2Ph, which were tested before.[4,5] There is a difference, however, because the latter, due to their small size, are able to afford the 1,2,7-isomers of $Re_2Cl_5(PR_3)_3$ with two phosphines located cis to each other on one of the rhenium atoms. In contrast, the increased cone angles of the PEt_3 and PPr^n_3 ligands militate against the formation of 1,2,7-$Re_2Cl_5(PR_3)_3$ molecules, even under mild conditions, confirming the observations made in our previous experiments about the impossibility of obtaining the latter compounds with any phosphines other than PMe_3 and PMe_2Ph.

The products **1a** and **2a** are both different from those previously isolated in similar reactions, and different from each other. With PEt_3 we get **1a**, which contains the anion $[Re_2Cl_6(PEt_3)_2]^-$, while with PPr^n_3 we get a $Re_2Cl_5(PPr^n_3)_3$ neutral molecule which has a 1,3,6 distribution instead of a 1,2,7 distribution of the phosphine ligands. We believe that in both cases there is initial and rapid substitution of two Cl^- by PR_3 to give a $Re_2Cl_6(PR_3)_2$ intermediate. With PPr^n_3 this remains in solution and rapidly undergoes further substitution and reduction (either in that order or the reverse) to give **2a** as the final product. With PEt_3 the $Re_2Cl_6(PEt_3)_2$ precipitates and is then slowly and heterogeneously reduced to give the $[Re_2Cl_6(PEt_3)_2]^-$, ion which is ultimately isolated with the $[Bu^n_4N]^+$ counterion.

In benzene media, the interaction of the $[Re_2Cl_8]^{2-}$ with triethyl- and tri-*n*-propylphosphines proceeds in a completely different manner than it does in propanol. In addition to the reduced dirhenium products **1a** and **2a** mentioned above, we isolated mononuclear Re^{IV} complexes $ReCl_4(PR_3)_2$ ($PR_3 = PEt_3$ (**1b**) and PPr^n_3 (**2b**)). This shows that reactions are disproportionations according to the following scheme: $3Re_2^{6+} \rightarrow 2Re_2^{5+} + 2Re^{4+}$. At room temperature these reactions are very slow and they require some heating to accelerate the transformation process. The reaction equations may be written as follows in the case of PEt_3 (eq 1) and PPr^n_3 (eq 2), respectively:

$$3[Bu^n_4N]_2[Re_2Cl_8] + 8PEt_3 \rightarrow 2[Bu^n_4N][Re_2Cl_6(PEt_3)_2] + 2ReCl_4(PEt_3)_2 + 4[Bu^n_4N]Cl \quad (1)$$

$$3[Bu^n_4N]_2[Re_2Cl_8] + 10PPr^n_3 \rightarrow 2Re_2Cl_5(PPr^n_3)_3 + 2ReCl_4(PPr^n_3)_2 + 6[Bu^n_4N]Cl \quad (2)$$

The disproportionation mechanism for the reactions of $[Re_2Cl_8]^{2-}$ with phosphines is observed here not for the first time. Recently we published[7] the results of our investigation on the interaction of $[Re_2Cl_8]^{2-}$ with diethylphosphine, PEt_2H, which also involved a different disproportionation of the type $2Re_2^{6+} \rightarrow Re_2^{8+} + Re_2^{4+}$ and was found to proceed according to the equation

$$2[Bu^n_4N]_2[Re_2Cl_8] + 10PEt_2H \rightarrow Re_2Cl_4(PEt_2H)_4 + [Bu^n_4N][Re_2(\mu\text{-}PEt_2)_3Cl_6] + 3[Bu^n_4N]Cl + 3[PEt_2H_2]Cl \quad (3)$$

We observed[17] still another disproportionation process, $3Re_2^{6+} \rightarrow Re_2^{8+} + 2Re_2^{5+}$, with another secondary phosphine ligand, namely, PCy_2H, with both dirhenium products being isolated and characterized:

$$3[Bu^n_4N]_2[Re_2Cl_8] + 12PCy_2H \rightarrow 2Re_2Cl_5(PCy_2H)_3 + [Bu^n_4N][Re_2(\mu\text{-}PCy_2)_3Cl_6] + 5[Bu^n_4N]Cl + 3[PCy_2H_2]Cl \quad (4)$$

In the latter two cases secondary phosphines are deprotonated and form the phosphido bridges, thus giving the $Re^{IV}-Re^{IV}$ dinuclear face-sharing complexes of the type $[Re_2(\mu\text{-}PR_2)_3Cl_6]^-$

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(15) Crystal data for 1,3,6-$Re_2Cl_5(PPr^n_3)_3$: orthorhombic, $P2_12_12_1$ (No. 19), $a = 12.214(2)$ Å, $b = 15.296(2)$ Å, $c = 20.945(6)$ Å, $V = 3913(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.749$ g cm^{-3}, $T = -120$ °C, full-matrix refinement on F^2 (Enraf-Nonius CAD-4S, SHELXL-93), R1 (on F_o) = 0.0526, wR2 (on F_o^2) = 0.1231, GOF = 1.086 for 363 parameters and 4 restraints, 5033 unique data (4494 with $I > 2\sigma(I)$). Re−Re = 2.220(1) Å. Percentage occupancies for dirhenium unit disorder: 76.1%, 20.8%, and 3.1%. See Supporting Information for other structure details.

(16) Crystal data for *trans*-$ReCl_4(PEt_3)_2$: orthorhombic, *Pbca* (No. 61), $a = 12.876(2)$ Å, $b = 12.1351(7)$ Å, $c = 13.2125(7)$ Å, $V = 2064.5(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.816$ g cm^{-3}, $T = -60$ °C, full-matrix refinement on F^2 (Nonius FAST area detector, SHELXL-93), R1 (on F_o) = 0.0333, wR2 (on F_o^2) = 0.0817, GOF = 1.126 for 148 parameters, 1343 unique data (1139 with $I > 2\sigma(I)$). See Supporting Information for other structure details.

(17) Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. Manuscript in preparation.

Table 2. Electrochemical Data[a] for the Species in the $[Re_2Cl_8]^{2-}$−PEt_3 System

complex	$E_{1/2}$(red)	$E_{1/2}$(ox)(1)	$E_{1/2}$(ox)(2)
$ReCl_4(PEt_3)_2$	−0.33		
$Re_2Cl_6(PEt_3)_2$	−0.08		
$Re_2Cl_5(PEt_3)_3$	−0.85	+0.37	
$Re_2Cl_4(PEt_3)_4$[b]		−0.42	+0.80
$[Re_2Cl_8]^{2-}$	−0.87	+1.21	
[intermediate]		+0.58	

[a] Unless otherwise stated, data are in volts vs Ag/AgCl in CH_2Cl_2−0.1 M TBAH as supporting electrolyte at room temperature. [b] Data from ref 8b; in volts vs SSCE in CH_2Cl_2−0.2 M TBAH.

Table 3. −FAB/DIP Mass Spectrum[a]of the Initial Product of the Reaction between $[Re_2Cl_8]^{2-}$ and PEt_3 in Benzene

anion	*m*/*z*	*I* (%)
$[Re_2Cl_7(PEt_3)_3]^-$	973	2
$[Re_2Cl_6(PEt_3)_3]^-$	937	17
$[Re_2Cl_7(PEt_3)_2]^-$	856	10
$[Re_2Cl_6(PEt_3)_2]^-$	822	47
$[Re_2Cl_7(PEt_3)]^-$	736	8
$[Re_2Cl_6(PEt_3)]^-$	702	100
$[Re_2Cl_5(PEt_3)]^-$	670	28
$[Re_2Cl_7]^-$	621	9
$[Re_2Cl_6]^-$	584	65
$[Re_2Cl_5]^-$	549	29

[a] In CH_2Cl_2 solution with an NBA matrix.

in contrast to mononuclear Re^{IV} compounds isolated with tertiary phosphine ligands in the present work.

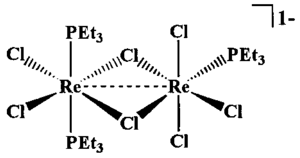
The results obtained demonstrate that the disproportionation of the dirhenium(III) complexes is not a rare process and can occur, albeit with different stoichiometries, whenever the reaction conditions are neither reductive nor oxidative. This raises the question as to what are the initial products of interaction between the octachlorodirhenate and phosphines, which then undergo disproportionation. We found earlier[6] that, when trimethylphosphine reacts with the $[Re_2Cl_8]^{2-}$ in benzene, the intermediate product could be isolated as an edge-sharing bioctahedral complex $Re_2(\mu\text{-}Cl)_2Cl_4(PMe_3)_4$ which has no metal−metal bond. An analogous paramagnetic compound has been suggested[7] for the reaction of the $[Re_2Cl_8]^{2-}$ with diethylphosphine.

We have made special efforts to detect such initial products for the phosphines studied here. Although all of our attempts to isolate intermediate complexes in the solid state have failed, we were able to show their presence in solution. The most reliable data have been obtained for the interaction of $[Re_2Cl_8]^{2-}$ with PEt_3 in benzene.

An initial paramagnetic ($g = 2.77$, CH_2Cl_2, 100 K) product of the reaction between $[Re_2Cl_8]^{2-}$ and PEt_3 in benzene starts to decompose and to produce $[Re_2Cl_6(PEt_3)_2]^-$ (**1a**) and $ReCl_4(PEt_3)_2$ (**1b**) immediately after its formation. While the less soluble **1a** is crystallizing out, the solution always contains some amount of **1b**. Voltammetric studies on this solution reveal two reversible waves, one of which (at −0.33 V) corresponds to the $[ReCl_4(PEt_3)_2]^{0/-1}$ reduction of **1b** (this was later confirmed on a pure sample) and another one (at +0.58 V) which does not belong to any known species in the $[Re_2Cl_8]^{2-}$−PEt_3 system (Table 2). The negative FAB/DIP mass spectrum of this solution gives a very informative pattern containing a series of peaks corresponding to the dirhenium anions with seven chlorides and/or three triethylphosphine groups, beginning with the $[Re_2Cl_7(PEt_3)_3]^-$ ($m/z = 973$) signal (Table 3).

The data obtained allow us to write down the formula of the dirhenium(III) intermediate as a tetrabutylammonium salt of the $[Re_2Cl_7(PEt_3)_3]^-$ anion (**1c**), to which we assign an edge-sharing bioctahedral core structure (Chart 1). In this case its formation can be simply described as

Chart 1



$$[Bu^n_4N]_2[Re_2Cl_8] + 3PEt_3 \rightarrow [Bu^n_4N][Re_2Cl_7(PEt_3)_3] + [Bu^n_4N]Cl \quad (5)$$

and its disproportionation to **1a** and **1b** can be written as

$$3[Bu^n_4N][Re_2Cl_7(PEt_3)_3] \rightarrow 2[Bu^n_4N][Re_2Cl_6(PEt_3)_2] + 2ReCl_4(PEt_3)_2 + [Bu^n_4N]Cl + PEt_3 \quad (6)$$

We made several attempts to crystallize **1c** from different solvent mixtures, but always ended up with the products **1a** and **1b**. Interestingly, if we treat the intermediate **1c** with warm hexanes, we can force its decomposition according to a route which is slightly different from that in other solvents:

$$3[Bu^n_4N][Re_2Cl_7(PEt_3)_3] \rightarrow [Bu^n_4N][Re_2Cl_6(PEt_3)_2] + Re_2Cl_5(PEt_3)_3 + 2ReCl_4(PEt_3)_2 + 2[Bu^n_4N]Cl \quad (7)$$

In this case neutral complexes $Re_2Cl_5(PEt_3)_3$[18] and **1b** are soluble in hexanes and can thus be separated from the insoluble ionic product **1a**.

We do not have clear evidence for the existence of the intermediate complex with PPr^n_3, but we believe that the mechanism of the transformation could be similar. The initial product of the reaction with tri-*n*-propylphosphine is evidently less stable than **1c** and can be regarded as a neutral molecule, $Re_2Cl_6(PPr^n_3)_4$ (**2c**). Its decomposition to **2a** and **2b** may be written as

$$3Re_2Cl_6(PPr^n_3)_4 \rightarrow 2Re_2Cl_5(PPr^n_3)_3 + 2ReCl_4(PPr^n_3)_2 + 2PPr^n_3 \quad (8)$$

Molecular Structures. $[Bu^n_4N][Re_2Cl_6(PEt_3)_2]$ (**1a**) is the first example of a characterized compound with this stoichiometry among the dirhenium(II,III) species. The central part of the structure, the dinuclear anionic complex (Figure 1), corresponds almost exactly in all geometric characteristics to its neutral non-disordered Re^{III}−Re^{III} counterpart described[8a] many years ago. The dirhenium anion resides on an inversion center to give an eclipsed geometry with C_{2h} symmetry. The arrangement of PEt_3 ligands corresponds to the so-called 1,7-isomer of the $Re_2Cl_6P_2$ core type, the only known so far. Although we have failed to get a good convergence in the refinement of **1a** because of twinning problems, the structure of the complex is well-established and fully confirmed by the data of elemental analysis and mass and ESR spectroscopy.

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[18] (a) For 1,3,6-$Re_2Cl_5(PEt_3)_3$, CV (CH_2Cl_2, 22 °C, V vs Ag/AgCl): $E_{1/2}(\text{red}) = -0.85$, $E_{1/2}(\text{ox}) = +0.37$. + FAB/DIP-MS (NBA/$CH_2Cl_2$, *m*/*z*): 903 ($[M]^+$), 868 ($[M - Cl]^+$), 785 ($[M - PEt_3]^+$), 750 ($[M - Cl - PEt_3]^+$), 667 ($[M - 2PEt_3]^+$). (b) For the crystal structure, see: Cotton, F. A.; Price, A. C.; Vidyasagar, K. *Inorg. Chem.* **1990**, *29*, 5143.

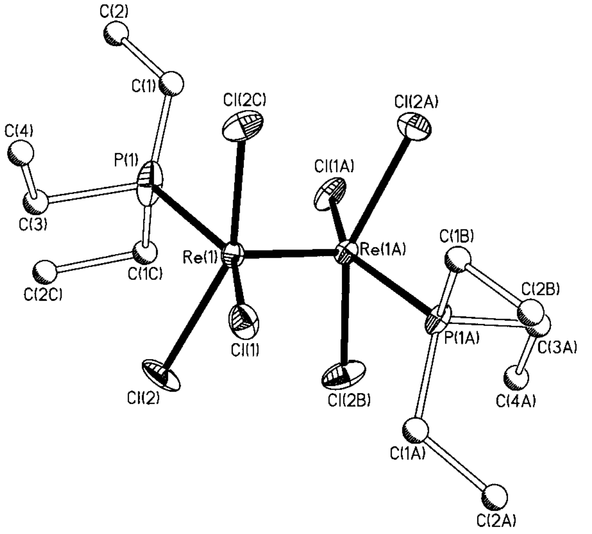

Figure 1. Perspective drawing of the $[Re_2Cl_6(PEt_3)_2]^-$ anion from **1a**. Atoms are represented by thermal ellipsoids at the 30% probability level. Carbon atoms are shown as spheres of an arbitrary radius. Hydrogen atoms are omitted.

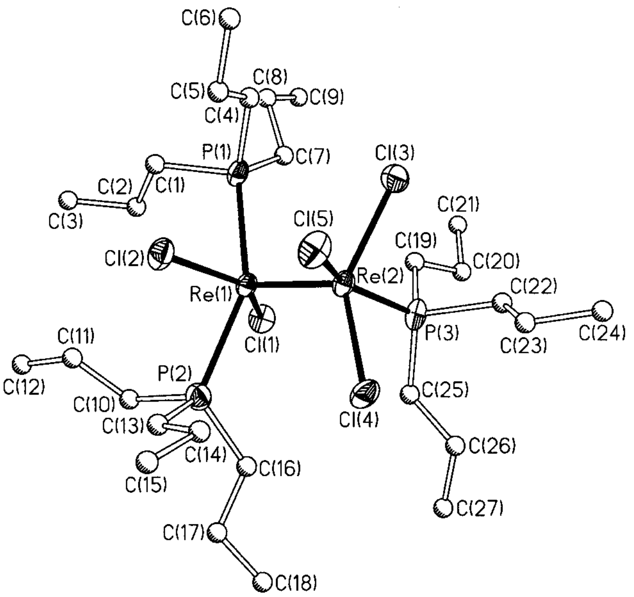

Figure 2. Perspective drawing of 1,3,6-$Re_2Cl_5(PPr^n_3)_3$ (**2a**). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon atoms are shown as spheres of an arbitrary radius. Hydrogen atoms are omitted.

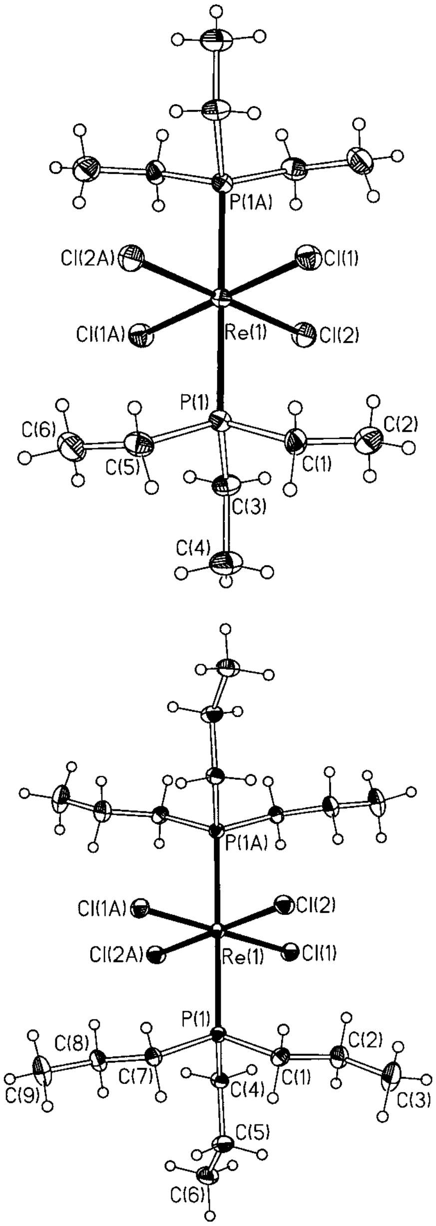

Figure 3. Perspective drawings of (a) *trans*-$ReCl_4(PEt_3)_2$ (**1b**) and (b) *trans*-$ReCl_4(PPr^n_3)_2$ (**2b**). Atoms are represented by thermal ellipsoids at the 40% probability level. Hydrogen atoms are shown as spheres of an arbitrary radius.

The $Re_2Cl_5(PPr^n_3)_3$ (**2a**) molecule (Figure 2) belongs to a large family of 1,3,6-isomers, $M_2Cl_5(PR_3)_3$ (M = Re, $PR_3 = PMe_3$,[18b] PEt_3,[18b] PMe_2Ph,[5] PCy_2H;[17] M = Tc, $PR_3 = PMe_2Ph$;[19] M = W, $PR_3 = PMe_3$[20]) having two phosphine groups trans to each other on one of the metal atoms. The Re−Re bond in **2a**, 2.2224(7) Å (Table 4), is typical for corresponding dirhenium molecules with a bond order of 3.5. In both polymorphic modifications of **2a** we always observed a three-way disorder of the dirhenium unit; for example, the percentage occupancies for the reported structure $\mathbf{2a}\cdot 0.25C_6H_{14}$ are 90.1%, 5.1%, and 4.8%. It should be noted that complex $Re_2Cl_5(PPr^n_3)_3$ was first obtained a long time ago by Walton et al.[21] by disproportionation of the dirhenium(II) compound $Re_2Cl_4(PPr^n_3)_4$ in ethanol.

The crystal structures of the mononuclear rhenium(IV) complexes $ReCl_4(PPr_3)_2$ ($PR_3 = PEt_3$ (**1b**) and PPr^n_3 (**2b**)) (Figure 3) were examined in order to conclusively identify the products from the disproportionation processes occurring in benzene. As do all other compounds of that composition,[22] the octahedral molecules **1**−**2b** possess a core structure of D_{4d} virtual symmetry owing to a trans location of phosphine ligands. All bond lengths and angles (Table 5) for these compounds are as expected. Another polymorph of **1b** was obtained before[22a] by a different synthetic method.

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Table 4. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for 1,3,6-$Re_2Cl_5(PPr^n_3)_3$·$0.25C_6H_{14}$ (**2a**·$0.25C_6H_{14}$)

Re(1)−Re(2)	2.2224(7)	Re(2)−P(3)	2.457(3)
Re(1)−P(1)	2.455(3)	Re(2)−Cl(3)	2.334(3)
Re(1)−P(2)	2.473(3)	Re(2)−Cl(4)	2.330(3)
Re(1)−Cl(1)	2.362(2)	Re(2)−Cl(5)	2.358(3)
Re(1)−Cl(2)	2.356(3)		
P(1)−Re(1)−P(2)	150.68(9)	P(3)−Re(2)−Cl(3)	83.5(1)
P(1)−Re(1)−Cl(1)	89.70(9)	P(3)−Re(2)−Cl(4)	85.9(1)
P(1)−Re(1)−Cl(2)	85.43(9)	P(3)−Re(2)−Cl(5)	155.4(1)
P(2)−Re(1)−Cl(1)	84.3(1)	Cl(3)−Re(2)−Cl(4)	141.1(1)
P(2)−Re(1)−Cl(2)	82.3(1)	Cl(3)−Re(2)−Cl(5)	87.8(1)
Cl(1)−Re(1)−Cl(2)	142.9(1)	Cl(4)−Re(2)−Cl(5)	86.6(1)
Re(2)−Re(1)−P(1)	102.35(7)	Re(1)−Re(2)−P(3)	101.06(7)
Re(2)−Re(1)−P(2)	106.59(7)	Re(1)−Re(2)−Cl(3)	110.69(7)
Re(2)−Re(1)−Cl(1)	111.21(7)	Re(1)−Re(2)−Cl(4)	108.08(7)
Re(2)−Re(1)−Cl(2)	105.78(7)	Re(1)−Re(2)−Cl(5)	103.50(7)
P(1)−Re(1)−Re(2)−Cl(3)	−4.0(1)	P(2)−Re(1)−Re(2)−Cl(4)	4.4(1)
Cl(1)−Re(1)−Re(2)−P(3)	3.4(1)	Cl(2)−Re(1)−Re(2)−Cl(5)	0.1(1)

Table 5. Selected Bond Distances (Å) and Angles (deg) for *trans*-$ReCl_4(PEt_3)_2$ (**1b**) and *trans*-$ReCl_4(PPr^n_3)_2$ (**2b**)

	1b	**2b**
Re(1)−Cl(1)	2.337(1)	2.334(1)
Re(1)−Cl(2)	2.335(1)	2.343(1)
Re(1)−P(1)	2.518(1)	2.513(1)
P(1)−Re(1)−Cl(1)	88.36(4), 91.64(4)	88.77(4), 91.23(4)
P(1)−Re(1)−Cl(2)	88.92(4), 91.09(4)	89.37(4), 90.63(4)
Cl(1)−Re(1)−Cl(2)	89.50(5), 90.50(5)	89.28(4), 90.73(4)

Concluding Remarks

The main point of the present study is an unambiguous proof that the nature of the solvent has a great influence on the reaction pathway. A one-electron reduction of $[Re_2Cl_8]^{2-}$ under mild conditions can take place even in the presence of PEt_3 and PPr^n_3 (not the most basic of phosphines), if the reaction medium is propanol. On the other hand, in benzene a disproportionation process rather than reduction occurs for the same phosphine ligands. These results give evidence for the hypothesis that the solvent itself is the actual reducing agent. However, C_3H_7OH cannot be conclusively identified as the reducing agent until its oxidized form, propionaldehyde, can be found among the reaction products. This has not been done so far. Reactions of $[Re_2Cl_8]^{2-}$ with other phosphines in benzene, where only reduced products have been found,[5,6] need to be re-examined for the presence of the oxidized rhenium species.

Another interesting result of this investigation is the evidence obtained for the occurrence of an intermediate complex in the course of disproportionation reactions in solution. It is clear now that face- and edge-sharing complexes having 9 and 10 ligands, respectively, attached to the dirhenium unit play an important role in all processes involving mixed chloride/phosphine species. Thus, recently we found[23] a face-sharing dirhenium(II,III) compound $Re_2(\mu\text{-}Cl)_3Cl_2(PMe_3)_4$ which is likely to be an intermediate for the cis−trans isomerization that occurs in going from 1,2,7-$Re_2Cl_5(PMe_3)_3$ to $[1,3,6,8\text{-}Re_2Cl_4(PMe_3)_4]^+$. More studies on the subject of intermediate complexes are currently underway.

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Supporting Information Available: Five X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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