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Mixed Chloride/Phosphine Complexes of the Dirhenium Core. 3. Novel Structures with Diethylphosphido-bridges and Terminal Diethylphosphines

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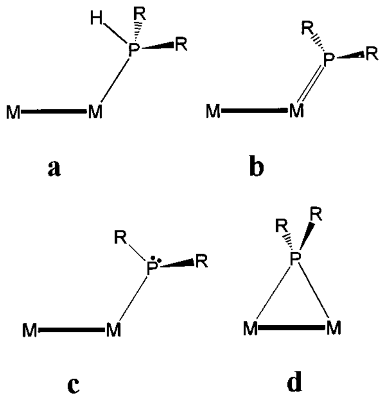
The interaction between octachlorodirhenium anions and diethylphosphine has been shown to strongly depend on reaction conditions, mainly the nature of the solvent and the amount of phosphine. As a result, novel dirhenium products with oxidation states ranging from Re^{II} to Re^{IV} have been obtained. The reaction of $[Re_2Cl_8]^{2-}$ with an excess of PEt_2H in dichloromethane or acetonitrile led to the first example of a face-sharing complex of rhenium(IV) with three phosphido-bridges, namely $[Bu^n_4N][Re_2(\mu\text{-}PEt_2)_3Cl_6]$ (**1**). The unusual edge-sharing $Re_2(\mu\text{-}PEt_2)_2Cl_4(PEt_2H)_4$ (**2**) complex of rhenium(III) with C_i core symmetry, containing both terminal phosphines and phosphido-bridges, has been obtained by carrying out the reaction with an excess of PEt_2H in a benzene (or propanol) − HCl mixture at room temperature. A new example of the 1,2,7,8-type of dirhenium(II) complex, $Re_2Cl_4(PEt_2H)_4$ (**3**), having diethylphosphine ligands located cis on each Re atom, has been isolated from the reaction of $[Re_2Cl_8]^{2-}$ with PEt_2H in an ethanol-HCl medium. The solid-state structures of complexes **1**−**3** have been investigated by X-ray crystallography. Complexes **1** and **2** both crystallized in two forms: $[Bu^n_4N][Re_2(\mu\text{-}PEt_2)_3Cl_6]$ **1a**, $P2_1/n$ with $a = 10.482(1)$ Å, $b = 16.512(2)$ Å, $c = 23.986(2)$ Å, $\beta = 93.637(8)°$, and $Z = 4$; $[Bu^n_4N][Re_2(\mu\text{-}PEt_2)_3Cl_6]\cdot 1.5\ C_7H_8$ **1b**, $C2/c$ with $a = 38.746(9)$ Å, $b = 10.322(2)$ Å, $c = 27.277(3)$ Å, $\beta = 110.35(1)°$, and $Z = 8$; $Re_2(\mu\text{-}PEt_2)_2Cl_4(PEt_2H)_4$ **2a**, $P2_1/n$ with $a = 11.081(3)$ Å, $b = 11.029(3)$ Å, $c = 15.627(2)$ Å, $\beta = 90.05(1)°$, and $Z = 2$; **2b**, $P2_1/c$ with $a = 16.094(3)$ Å, $b = 15.193(3)$ Å, $c = 15.548(3)$ Å, $\beta = 100.98(3)°$, and $Z = 4$. X-ray data for complex $Re_2Cl_4(PEt_2H)_4$ **3** are as follows: $P2_1/n$ with $a = 10.445(2)$ Å, $b = 10.113(3)$ Å, $c = 13.473(2)$ Å, $\beta = 102.17(2)°$, and $Z = 2$. Three bridging $\mu\text{-}PEt_2$ groups in the face-sharing complex **1** span a short metal−metal distance of 2.4060(6) Å, averaged over **1a** and **1b**, with a small $Re-PEt_2-Re$ angle of 61.34(7)°. The rhenium−rhenium bond length in the edge−sharing complex **2** is 2.7545(7) Å, averaged over **2a** and **2b**, while the bridging $Re-PEt_2-Re$ angle is 72.16(6)°, and the P−Re−P angle for the terminal phosphine ligands is 87.11(7)°. The Re−Re bond distance in **3**, 2.2533(8) Å, is typical for triply bonded dirhenium complexes, and the P−Re−P angle for the cis phosphine groups is 93.12(6)°.

Introduction

In the course of studying the reactions of the octachlorodirhenium anion, $[Re_2Cl_8]^{2-}$, with two small and basic tertiary phosphines, PMe_3 and PMe_2Ph, we have isolated a variety of products depending on the solvent used and other experimental conditions employed.[1,2] These two monodentate phosphines were shown to afford $Re_2Cl_4(PR_3)_4$ products with an unprecedented *cis*-coordination at the rhenium centers (1,2,7,8-isomers), in addition to complexes with the well-known *trans*-geometry (1,3,6,8-isomers). In the course of searching for other phosphines with small cone angles we have selected diethylphosphine, PEt_2H. Several coordination modes are known for this secondary phosphine. It can be coordinated to a metal atom in the same manner as tertiary phosphines in the form of a neutral terminal phosphine ligand[3] (Chart 1a). Moreover, P−M−P angles were found[3b] to be around 92° for such coordination, which means a *cis*-type of arrangement is possible for PEt_2H. At the same time deprotonation of diethylphosphine often occurs even at room-temperature resulting in the formation of compounds with terminal and bridging diethylphosphido ligands (Chart 1b−d). Terminal phosphido groups, in turn, are known[4] to be coordinated in two ways: with a double (or partial double) metal-to-phosphorus bond (Chart 1b) and with a single M−P bond and a lone electron pair on the P atom (Chart 1c).

Chart 1



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However, the best known is a bridging μ-PEt$_2$ mode (Chart 1d), which can span metal−metal distances from 2.68 to 3.72 Å, while M-PEt$_2$−M angles range from 71.9 to 90.8°.[3a,b,5,6] This reflects the structural flexibility of the μ-PEt$_2$ group, allowing both bonding and nonbonding metal−metal arrangements as reported for the several homo-[3b,5] and hetero-polynuclear[3a,6] transition metal complexes.

Our results on the reactions of $[Re_2Cl_8]^{2-}$ with PEt$_2$H are in agreement with the expected behavior for a secondary phosphine. We observed the strong influence of the reaction conditions, mainly the nature of the solvent and the amount of phosphine, on the reaction pathway. By changing and controlling conditions we were able to isolate several new dirhenium products ranging from Re^{II} to Re^{IV}, unusual in both their compositions and stereochemistries. We present here the synthetic methods and the crystal structures of a face-sharing bioctahedral (FSBO) complex of Re^{IV}, $[Bu^n_4N][Re_2(\mu\text{-}PEt_2)_3Cl_6]$ (**1**); an edge-sharing bioctahedral (ESBO) complex of Re^{III}, $Re_2(\mu\text{-}PEt_2)_2Cl_4(PEt_2H)_4$ (**2**); and a triply bonded Re^{II} complex, $Re_2Cl_4(PEt_2H)_4$ (**3**).

Compounds **1** and **2** are different from all other known dirhenium FSBO and ESBO complexes. For example, the dirhenium anion in **1** is the first example of a face-sharing complex with three phosphido bridging groups and only the second Re^{IV} FSBO species. The complex $Re_2(\mu\text{-}PEt_2)_2Cl_4(PEt_2H)_4$ (**2**), only the second ESBO species for rhenium with monodentate phosphines, displays for the first time a C_i type of symmetry with a *cis*-disposition of PEt$_2$H ligands. Complex **3** expands a newly-opened[1,2] class of a *cis*,*cis*-geometry (1,2,7,8) for the $Re_2Cl_4(PR_3)_4$ stoichiometry to include secondary phosphines.

Experimental Section

General Procedures. All 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$_2$H, Strem Chemicals; $[Bu^n_4N]_2[Re_2Cl_8]$, Aldrich, Inc. Chloroform-d_1 and benzene-d_6 were obtained from Cambridge Isotope Laboratories.

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 done with the use of Bioanalytical Systems Inc. electrochemical analyzer, model 100. The scan rate was 100 mV/s at a Pt disk electrode. The electronic absorption spectra in CH$_2$Cl$_2$ were recorded on a Cary 17D spectrophotometer. The $^{31}P\{^1H\}$ NMR data were recorded at room temperature on a UNITY-plus 300 multinuclear spectrometer operated at 121.4 MHz and using 85% H$_3$PO$_4$ as an external standard. Elemental analyses were done on compounds **1a** and **2a** by Canadian Microanalytical Services, Ltd.

Synthesis of $[Bu^n_4N][Re_2(\mu\text{-}PEt_2)_3Cl_6]$ (1). Method 1. $[Bu^n_4N]_2[Re_2Cl_8]$ (0.103 g, 0.09 mmol) was suspended in a mixture of 1-propanol (8 mL) with 1 mL of diethylphosphine. The reaction mixture was stirred at room temperature for 12 h, resulting in a red-brown solution. The solvent and the excess of phosphine were then removed by vacuum distillation to leave an oily brown residue. This was dissolved in 10 mL of dichloromethane and refluxed (~40 °C) for 24 h. The solvent was then removed under reduced pressure to give a brown solid, which was dissolved in 5 mL of CH$_2$Cl$_2$ and the solution carefully layered with 5 mL of hexanes. After a few days, large, brown-purple block-shaped crystals of **1a** grew on the walls of the Schlenk tube. Yield: 0.034 g (36%).

Method 2. A 1 mL amount of PEt$_2$H was added to the solution containing 0.115 g (0.1 mmol) of $[Bu^n_4N]_2[Re_2Cl_8]$ in 15 mL of acetonitrile. The color of the solution immediately turned brown. After stirring the solution for 1 h at room temperature the solvent was removed under reduced pressure leaving a brown solid, which was washed with hexanes (2 × 10 mL), dried, and then dissolved in 10 mL of toluene. The red-violet, block-shaped crystals of **1b** were obtained by slow crystallization from toluene at −30 °C. Yield: 0.106 g (89%). Anal. Calcd for $Re_2Cl_6P_3N_1C_{28}H_{66}$ (**1a**): C, 30.72; H, 6.08; N, 1.28. Found: C, 30.58; H, 6.01; N, 1.60. $^{31}P\{^1H\}$ NMR (CDCl$_3$, 23 °C): δ 247.1 (s). CV (CH$_2$Cl$_2$, 22 °C, V vs Ag/AgCl): $E_{1/2}(\text{red}) = -0.69$; $E_{1/2}(\text{ox})$ (irr) $= +1.02$.

Synthesis of $Re_2(\mu\text{-}PEt_2)_2Cl_4(PEt_2H)_4$ (2). Method 1. To a suspension containing 0.170 g (0.15 mmol) of $[Bu^n_4N]_2[Re_2Cl_8]$ in 20 mL of benzene was added 1 mL of PEt$_2$H. The mixture was stirred over 70 h at room temperature until the color of the solution turned brown. It was then filtered leaving some unreacted starting material at the frit. The solvent was removed from the brown filtrate under reduced pressure to yield a crystalline brown solid. This was washed with hexanes (2 × 15 mL), dried in a vacuum and then extracted with 12 mL of benzene. After filtration the benzene solution was layered with 20 mL of hexanes affording red-brown plates of **2a** in 4 days. This material was contaminated by a few red-brown, needle-shaped crystals having a unit cell identical with that of the compound **1a** (vide infra) and separated from **2** manually. Yield: 0.092 g (59%).

Method 2. To a suspension containing 0.115 g (0.1 mmol) of $[Bu^n_4N]_2[Re_2Cl_8]$ in 10 mL of 1-propanol was added 0.3 mL of concentrated HCl followed by 0.8 mL of PEt$_2$H. The mixture was stirred 1 h at room temperature until the color turned dark brown. The solvent was removed under reduced pressure to leave a brown oily residue. This was dissolved in 8 mL of toluene, and the solution was layered with 15 mL of hexanes. The red-brown needles of **2b** came out in a few hours. Yield: 0.081 g (75%).

Method 3. To a suspension containing 0.115 g (0.1 mmol) of $[Bu^n_4N]_2[Re_2Cl_8]$ in 15 mL of benzene was added 0.5 mL of concentrated HCl followed by 0.8 mL of PEt$_2$H. The mixture was stirred about 90 h at room temperature to give a brown solution. A very small amount of unreacted starting material was separated from the solution by filtration. The solvent was then removed from the filtrate leaving a brown crystalline residue, which was washed with hexanes (2 × 10 mL), dried in a vacuum, and dissolved in 10 mL of toluene. The solution was layered with 20 mL of hexanes, yielding needle-shaped crystals of **2b** in a day. Yield: 0.067 g (63%). Anal. Calcd for $Re_2Cl_4P_6C_{24}H_{64}$ (**2a**): C, 27.38; H, 6.13. Found: C, 27.04; H, 5.98. $^{31}P\{^1H\}$ NMR (C$_6$D$_6$, 19 °C): δ −62.3 (m); −47.4 (m); −3.5 (m); −2.8 (m); 63.6 (m); 69.5 (m).

1,2,7,8-$Re_2Cl_4(PEt_2H)_4$ (3). To a suspension containing 0.115 g (0.1 mmol) of $[Bu^n_4N]_2[Re_2Cl_8]$ in 25 mL of ethanol was added a few drops of concentrated HCl. The mixture was cooled to 0 °C, and 0.1 mL of PEt$_2$H was syringed into the suspension, which was stirred 4 h at 0 °C, and then slowly warmed to room temperature. The resulting green solid was separated by filtration from the red-brown solution, washed with hexanes (2 × 10 mL), and dried in a vacuum. The solid was then dissolved in 7 mL of CH$_2$Cl$_2$, and the dichloromethane solution was layered with 12 mL of hexanes. The greenish-brown crystals of

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Table 1. Crystallographic Data for $[Bu^n_4N][Re_2(\mu\text{-}PEt_2)_3Cl_6]$ (**1a**), $[Bu^n_4N][Re_2(\mu\text{-}PEt_2)_3Cl_6]\cdot 1.5C_7H_8$ (**1b**), 1,2,5,6-$Re_2(\mu\text{-}PEt_2)_2Cl_4(PEt_2H)_4$ (**2a**,**b**), and 1,2,7,8-$Re_2Cl_4(PEt_2H)_4$ (**3**)

	1a	**1b**	**2a**	**2b**	**3**
formula	$Re_2Cl_6P_3N_1C_{28}H_{66}$	$Re_2Cl_6P_3N_1C_{38.5}H_{78}$	$Re_2Cl_4P_6C_{24}H_{64}$	$Re_2Cl_4P_6C_{24}H_{64}$	$Re_2Cl_4P_4C_{16}H_{44}$
fw	1094.83	1233.03	1052.77	1052.77	874.59
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	10.482(1)	38.746(9)	11.081(3)	16.094(3)	10.445(2)
b, Å	16.512(2)	10.322(2)	11.029(3)	15.193(3)	10.113(3)
c, Å	23.986(2)	27.277(3)	15.627(2)	15.548(3)	13.473(2)
β, deg	93.637(8)	110.35(1)	90.05(1)	100.98(3)	102.17(2)
V, Å^3	4143.1(7)	10228(3)	1909.8(8)	3732(1)	1391.2(5)
Z	4	8	2	4	2
ρ_{calc}, g cm^{-3}	1.755	1.601	1.831	1.874	2.088
μ, mm^{-1}	6.361	5.163	6.879	7.040	9.311
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, °C	−100	−60	−60	−60	−60
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.037 0.077	0.052 0.127	0.033 0.078	0.037 0.083	0.030 0.076
R1,[a] wR2[b] (all data)	0.091 0.090	0.065 0.142	0.039 0.083	0.047 0.090	0.031 0.079

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

3 came out in 3 days. Yield: 0.015 g (34%). The compound remaining in solution was shown to be complex **1**. Yield: 0.021 g (39%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 23 °C): δ 2.44 (s). CV (CH_2Cl_2, 22 °C, V vs Ag/AgCl): $E_{1/2}(ox)(1) = +0.03$, $E_{1/2}(ox)(2) = +1.14$.

X-ray Crystallographic Procedures. Single crystals of **1**−**3** were obtained as described above. In each case, a crystal of suitable quality was affixed to the end of a quartz fiber with grease in a cold nitrogen stream (−60 or −100 °C). X-ray diffraction experiments were carried out using one of the two fully automated diffractometers equipped with monochromated Mo Kα radiation (λ = 0.710 73 Å), Enraf-Nonius CAD-4S (**1a**) and Nonius FAST with an area detector (**1b**, **2a**,**b**, and **3**). Unit cell determination and data collection followed routine procedures and practices of this laboratory.[7] Oscillation photographs of principal axes were taken to confirm Laue class and axial lengths. All data were corrected for Lorentz and polarization effects.

All calculations were done on a DEC Alpha running VMS. The coordinates of rhenium atoms for all of the structures were found in direct-method *E* maps using the structure solution program SHELXTL.[8] The positions of the remaining atoms were located by use a combination of least-squares refinements and difference Fourier maps in the SHELXL-93 program.[9] In each case all hydrogen atoms connected to P atoms were refined independently with their own thermal parameters. All the other hydrogen atoms (connected to C atoms) were included at idealized positions for the structure factor calculations but not refined (except for **2a**). Details on data collection and structure refinement are reported in Table 1.

$[Bu^n_4N][Re_2(\mu\text{-}PEt_2)_3Cl_6]$ (1a). A brown-purple block of size 0.38 × 0.15 × 0.08 mm was selected for diffraction studies. Cell parameters consistent with those of a primitive monoclinic lattice were obtained by least-squares refinement of 25 centered reflections in the range $24 < 2\theta < 30°$. A total of 5751 unique data were collected for $4 < 2\theta < 46°$ using the $\omega-\theta$ scan technique. Three representative reflections were measured at regular intervals and showed no decay in diffraction intensity. An absorption correction based on azimuthal scans of eight reflections with Eulerian angle χ near 90° was applied to the data. Systematic absences in the data uniquely determined the space group to be $P2_1/n$. Anisotropic displacement parameters were assigned to all atoms, except hydrogen. Final least-squares refinement of 371 parameters converged with $R = 0.037$ (for 4103 reflections with $I > 2\sigma(I)$) and $R = 0.091$ (for all 5751 data). The only large peak in the final difference Fourier map had an electron density of 1.91 e/Å^3, lying 1.13 Å from the Re(1) atom.

$[Bu^n_4N][Re_2(\mu\text{-}PEt_2)_3Cl_6]\cdot 1.5\ C_7H_8$ (1b). A red-violet crystal with approximate dimensions of 0.20 × 0.20 × 0.08 mm was placed on the end of a glass fiber with silicone grease. Indexing based on 50 reflections resulted in a C-centered monoclinic lattice and cell parameters were further refined against 248 reflections in the range $12 < 2\theta < 42°$. No absorption correction was made. A total of 23 297 data were collected for $4 < 2\theta < 45°$. After averaging of equivalent reflections, a total of 6658 unique data remained. Examination of the systematic absences led to the selection of $C2/c$ as the space group. This choice was later confirmed by successful structure solution. After initial refinement of all atoms of the anion and tetrabutylammonium cation, it became apparent that two disordered molecules of toluene (one with a half-occupancy) were present in the asymmetric unit. All non-hydrogen atoms were refined with anisotropic displacement parameters except the disordered carbon atoms of the interstitial toluene molecules. Final least-squares refinement of 448 parameters resulted in residuals $R = 0.052$ (for 5526 reflections with $I > 2\sigma(I)$) and $R = 0.065$ (for all data). The highest peak in the final difference Fourier map was 2.01 e/Å^3 lying 1.38 Å from the Re(1) atom.

1,2,5,6-$Re_2(\mu\text{-}PEt_2)_2Cl_4(PEt_2H)_4$ (2a). A red-brown block of size 0.18 × 0.18 × 0.13 mm was used for diffraction studies. Unit cell parameters were obtained by refinement of 250 reflections in the range $18 < 2\theta < 42°$. By taking axial photos and analysis of intensity statistics the crystal was shown to belong to the monoclinic system despite the fact that the *a* and *b* parameters were pretty close to each other and all angles close to 90°. Data collection was carried out in the range $4 < 2\theta < 50°$. Systematic extinctions uniquely determined the space group as $P2_1/n$. All atoms, except hydrogen, were refined anisotropically. Hydrogen atoms connected to P and C atoms were found in a Fourier map and refined. Full refinement of 259 parameters resulted in residuals *R* based on 3002 reflections with $I > 2\sigma(I)$ and *R* based on all 3331 data of 0.033 and 0.039, respectively. The largest residual peak in the final difference electron density map was 1.39 e/Å^3, in the vicinity of the rhenium atoms.

2b. A red-brown needle with approximate dimensions 0.35 × 0.07 × 0.06 mm was mounted for intensity measurements. A primitive monoclinic cell was derived from the indexing of 50 reflections and was further refined using 250 reflections with $17 < 2\theta < 42°$. The structure was solved and refined in the space group $P2_1/c$. Final refinement, anisotropic for all non-hydrogen atoms, of 337 parameters converged with $R = 0.037$ (for 4100 reflections with $I > 2\sigma(I)$) and $R = 0.047$ for all 4879 data. A final difference Fourier map revealed that the highest remaining peak of electron density, 1.92 e/Å^3, was located 0.93 Å from the Re(2) atom.

1,2,7,8-$Re_2Cl_4(PEt_2H)_4$ (3). A greenish-brown crystal of almost cubic shape (0.25 × 0.23 × 0.20 mm) was mounted. Indexing based on 249 reflections with $16 < 2\theta < 42°$ gave a primitive monoclinic cell. Space group $P2_1/n$ was chosen for refinement. No metal nor ligand disorder was detected. After anisotropic refinement of all non-hydrogen atoms, H-atoms connected to P atoms were found in the

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difference Fourier map and were refined with their own thermal parameters. The other hydrogen atoms were placed in idealized positions. Final residuals were $R = 0.030$ (for 1708 reflections with $I > 2\sigma(I)$) and $R = 0.031$ (for all 1768 data). A final difference map revealed the highest peak, 1.78 e/Å^3, sitting 1.15 Å from the rhenium atom.

Results and Discussion

Chemical Aspects. Reaction of $[Re_2Cl_8]^{2-}$ with an excess of PEt_2H in dichloromethane affords the complex $[Bu^n_4N][Re_2(PEt_2)_3Cl_6]$ (**1**), with all phosphines coordinated in the deprotonated form as bridging phosphido ligands. The same reaction performed in acetonitrile proceeds even faster and gives higher yields of **1**. In these reactions Re^{III} is oxidized to Re^{IV}. A similar transformation has been observed before, namely, the oxidation of $[Re_2Cl_8]^{2-}$ to the $[Re_2Cl_9]^-$ anion,[10a] which is isoelectronic to that in **1**. Interestingly, the latter process has been seen in CH_2Cl_2 and CH_3CN reaction media, but with the use of Cl_2 as the oxidizing agent. In our case reaction proceeds without an additional oxidizer, in the presence of only diethylphosphine and solvent. It is very unlikely that PEt_2H can be the oxidizing agent in this reaction; it is better known as a reductant with transformation to P_2Et_4.[4] The following equation can be suggested for the reaction observed in dichloromethane:

$$[Bu^n_4N]_2[Re_2Cl_8] + 6PEt_2H + 2CH_2Cl_2 \rightarrow [Bu^n_4N][Re_2(PEt_2)_3Cl_6] + [Bu^n_4N]Cl + 3[PEt_2H_2]Cl + CH_2Cl{-}CH_2Cl \quad (1)$$

It is not obvious how to explain the process observed in acetonitrile, but the latter is also known to assist in oxidation reactions of metal complexes.

When octachlorodirhenate was reacted with an excess of PEt_2H in benzene, especially in the presence of HCl, deprotonation was slower and the oxidation was avoided. The product of the reaction in benzene is the rhenium(III) complex $Re_2(PEt_2)_2Cl_4(PEt_2H)_4$ (**2**), which has, along with two phosphido ligands, four neutral phosphine groups. It is worth noting here that the use of benzene as a solvent for the reaction of $[Re_2Cl_8]^{2-}$ with trimethylphosphine[1] also slowed the reduction process and afforded the edge-sharing dirhenium(III) complex $Re_2Cl_6(PMe_3)_4$. For some other monodentate phosphines as well, HCl was used[11] to obtain products of the type $Re_2Cl_6(PR_3)_2$ ($PR_3 = PEt_3$, PPr^n_3, PBu^n_3, PMe_2Ph, PEt_2Ph, $PMePh_2$, $PEtPh_2$, PPh_3).

The best conditions for the isolation of **2** appear to be the use of propanol as solvent in the presence of HCl. The reaction can be described by the following equation:

$$[Bu^n_4N]_2[Re_2Cl_8] + 8PEt_2H \rightarrow Re_2(PEt_2)_2Cl_4(PEt_2H)_4 + 2[Bu^n_4N]Cl + 2[PEt_2H_2]Cl \quad (2)$$

The dirhenium(II) complex $Re_2Cl_4(PEt_2H)_4$ (**3**) with only neutral phosphine groups present has been isolated when the reaction was performed in an ethanol−HCl medium without an excess of phosphine. In fact, this is the first case where $[Re_2Cl_8]^{2-}$ was converted to the Re_2^{4+} core compound by a phosphine at room temperature. Traditionally compounds of the $Re_2Cl_4(PR_3)_4$ ($PR_3 = PMe_3$, PEt_3, PPr^n_3, PBu^n_3, PMe_2Ph, PEt_2Ph) stoichiometry have been obtained by prolonged reflux of the mixture $[Re_2Cl_8]^{2-}{-}PR_3$ in alcohols[11c,12] or by assisted reduction with cobaltocene at room temperature.[1,2,11d] However, the present reaction is not a reduction of the Re atoms but rather a disproportionation process, as the second product isolated in the course of this reaction was the dirhenium(IV) complex **1**:

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

It is easy to see that reaction 3 requires only 5 equiv of the phosphine per one dirhenium unit, while for the formation of complexes **1** and **2**, 6 and 8 equiv of diethylphosphine are needed, respectively.

Comparison and analysis of these new reactions of $[Re_2Cl_8]^{2-}$ with PEt_2H confirm the general observation made for the tertiary phosphines, PMe_3[1] and PMe_2Ph,[2] namely, that the reaction route and the stoichiometry of the products depend strongly on the experimental conditions, mainly on the solvent used and the amount of phosphine. By controlling these factors it is possible to direct the reaction route and to obtain dirhenium complexes of different compositions. However, in contrast to tertiary phosphines, PEt_2H has the possibility of being deprotonated under similar experimental conditions, which gives additional stoichiometric variety in the resulting compounds. The oxidation to Re^{IV} is a new process that has never been observed before in corresponding reactions with tertiary phosphines.

We have not observed the deprotonation of diethylphosphine[3d] when the amine groups were exchanged with PEt_2H in complexes of the type $W_2Cl_4(NR_2)_2(NR_2H)_2$ (R = Et, Bu^n, Hex^n). In those substitution reactions, which proceed without change of formal oxidation state of W^{III}, PEt_2H was always coordinated as a terminal phosphine group. Recently[13] we succeeded in isolating a quadruple bonded $Mo_2Cl_4(PEt_2H)_4$ in nearly quantitative yield by replacing four diethylamine groups in the corresponding starting material. However, in cases where PEt_2H replaces not a neutral group, but an anionic ligand, Cl^- for instance, deprotonation is always a possibility, especially when the HCl can react with an excess of phosphine:

$$-Re{-}Cl + 2PEt_2H \rightarrow -Re{-}PEt_2 + [PEt_2H_2]Cl \quad (4)$$

Concerning the reaction mechanisms in all cases discussed above, three points have direct bearing: (i) There is a paramagnetic intermediate in the formation of **1** in propanol (method 1), as monitored by NMR. (ii) In the absence of an excess of phosphine there is a disproportionation of some intermediate compound to **1** and **3** (reaction 3). (iii) The previously reported[1] fact that the initial product of reaction between $[Re_2Cl_8]^{2-}$ and PMe_3 is the paramagnetic ESBO complex, $Re_2Cl_6(PMe_3)_4$. All these observations lead us to suggest that interaction of $[Re_2Cl_8]^{2-}$ with PEt_2H may initially afford the analogous edge-sharing product of composition "$Re_2Cl_6(PEt_2H)_4$" (**4**) (Scheme 1). Subsequent oxidation of **4** in CH_2Cl_2 and CH_3CN then results in the formation of **1** with full deprotonation of all coordinated phosphines. Replacement

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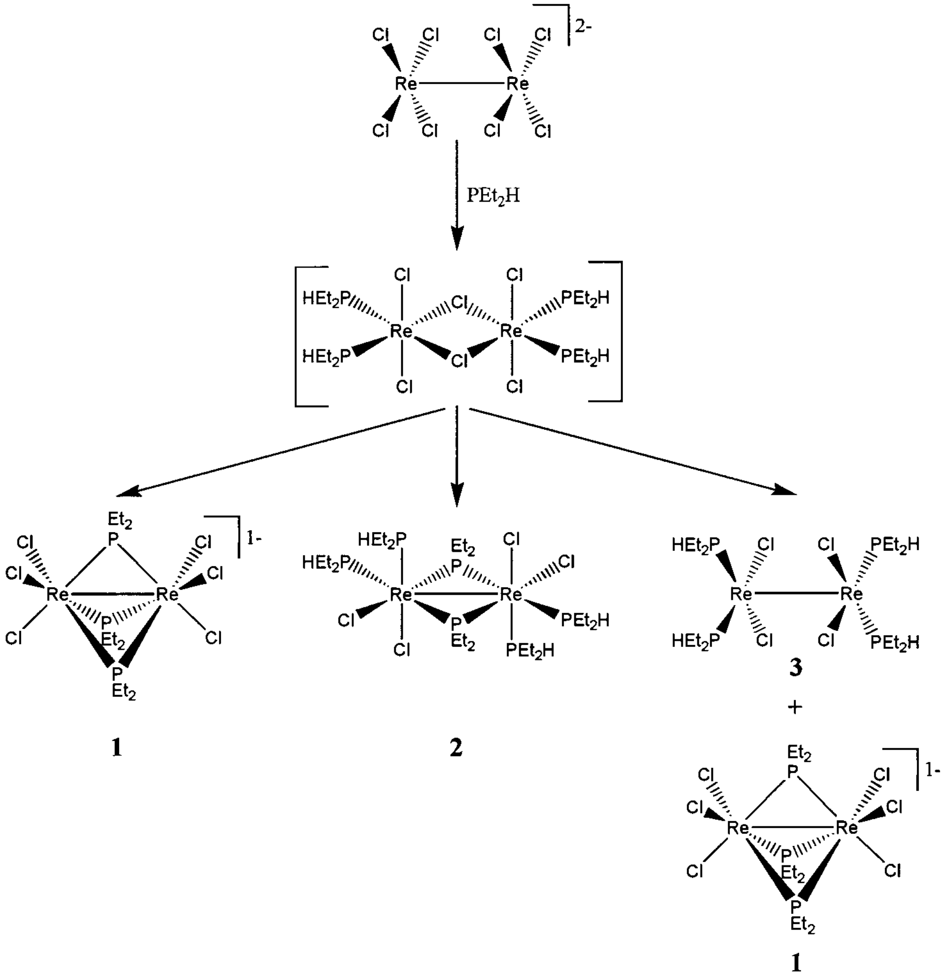
[10] (a) Heath, G. A.; McGrady, J. E.; Raptis, R. G.; Willis, A. C. *Inorg. Chem.* **1996**, *35*, 6838. (b) The analogous bromine anion, $[Re_2Br_9]^-$, was also mentioned to be under investigation with the Re−Re distance of 2.758(2) Å.

[11] (a) Cotton, F. A.; Curtis, N. F.; Robinson, W. R. *Inorg. Chem.* **1965**, *4*, 1696. (b) San Filippo, J., Jr. *Inorg. Chem.* **1972**, *11*, 3140. (c) Ebner, J. R.; Walton, R. A. *Inorg. Chem.* **1975**, *14*, 1987. (d) Dunbar, K. R.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 5.

[12] (a) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tomas, M.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 4950. (b) Root, D. R.; Blevins, C. H.; Lichtenberger, D. L.; Sattelberger, A. P.; Walton, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 953.

[13] Cotton, F. A.; Dikarev, E. V.; Herrero, S. *Inorg. Chem.* **1998**, in press.

Scheme 1



of two chloride bridges by phosphido ligands in **4** in the presence of an excess of PEt_2H and under the conditions unfavorable for oxidation gives **2** as the only product. In the absence of both phosphine and oxidative conditions the intermediate **4** may spontaneously disproportionate to **1** and **3**.

Stereochemical Aspects. $[Bu^n_4N][Re_2(\mu\text{-}PEt_2)_3Cl_6]$ (1). This compound crystallizes in the monoclinic space group $P2_1/n$ with four anions $[Re_2(\mu\text{-}PEt_2)_3Cl_6]^-$ and four tetra-*n*-butylammonium cations in the unit cell (**1a**). It was also isolated as a toluene solvate (**1b**) in the space group $C2/c$ with eight molecules of complex and twelve molecules of C_7H_8 per unit cell. The main part of the structure (Figure 1) consists of a face-sharing bioctahedral anion $[Re_2(\mu\text{-}PEt_2)_3Cl_6]^-$, in which two rhenium(IV) atoms are bridged by diethylphosphido groups, with three terminal chloride ligands completing the coordination sphere of each metal center. The dirhenium molecule does not have any crystallographically imposed symmetry, but the core has approximate D_{3h} symmetry with the principal axis passing along the metal−metal vector.

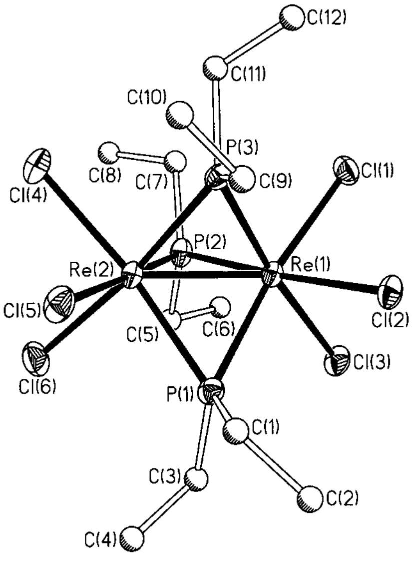


Figure 1. Perspective drawing of the $[Re_2(\mu\text{-}PEt_2)_3Cl_6]^-$ anion from **1a**. Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon atoms are shown as spheres of arbitrary radius. Hydrogen atoms are omitted.

The dirhenium anion in **1** represents just the third example of a complex where two transition metal atoms are bridged by three dialkylphosphido groups, but the other two[14] are not FSBO type compounds. Despite the fact that face-sharing bioctahedral complexes with d^3-d^3 electronic configurations are, probably, the best known[15] and include those of Nb^{II}, Ta^{II}, Cr^{III}, Mo^{III}, and W^{III}, the only example in that series for Re^{IV} was recently reported: $[Re_2Cl_9]^-$.[10a,b] The Re−Re distance in this paramagnetic compound is 2.704(1) Å. In sharp contrast, the isoelec-

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[14] (a) Budzichowski, T. A.; Chisholm, M. H.; Martin, J. D.; Huffman, J. C.; Moodley, K. G.; Streib, W. E. *Polyhedron* **1993**, *12*, 343. (b) Hey-Hawkins, E.; Fromm, K. *Polyhedron* **1995**, *14*, 2027.

[15] Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*, 2nd ed.; Oxford University Press: New York, 1993.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Re_2(\mu\text{-}PEt_2)_3Cl_6]^-$ Anion in **1a** and **1b**

		1a	**1b**
M−M	Re(1)−Re(2)	2.4023(6)	2.4097(6)
M−(*μ*-P)	Re(1)−P(1)	2.355(3)	2.372(3)
	Re(1)−P(2)	2.352(3)	2.361(3)
	Re(1)−P(3)	2.358(3)	2.358(3)
	Re(2)−P(1)	2.356(3)	2.357(3)
	Re(2)−P(2)	2.354(3)	2.364(3)
	Re(2)−P(3)	2.358(3)	2.354(3)
M−Cl	Re(1)−Cl(1)	2.430(3)	2.451(3)
	Re(1)−Cl(2)	2.444(2)	2.431(3)
	Re(1)−Cl(3)	2.428(2)	2.434(3)
	Re(2)−Cl(4)	2.432(3)	2.435(3)
	Re(2)−Cl(5)	2.426(3)	2.442(2)
	Re(2)−Cl(6)	2.417(3)	2.436(3)
(*μ*-P)−M−(*μ*-P)	P(1)−Re(1)−P(2)	96.8(1)	96.30(9)
	P(1)−Re(1)−P(3)	96.70(9)	96.08(9)
	P(2)−Re(1)−P(3)	95.53(9)	96.0(1)
	P(1)−Re(2)−P(2)	96.71(9)	96.6(1)
	P(1)−Re(2)−P(3)	96.65(9)	96.63(9)
	P(2)−Re(2)−P(3)	95.44(9)	96.04(9)
(*μ*-P)−M−Cl	P(1)−Re(1)−Cl(1)	172.68(9)	173.6(1)
	P(1)−Re(1)−Cl(2)	89.34(9)	90.6(1)
	P(1)−Re(1)−Cl(3)	86.52(9)	86.88(9)
	P(2)−Re(1)−Cl(1)	86.90(9)	86.8(1)
	P(2)−Re(1)−Cl(2)	172.61(9)	171.1(1)
	P(2)−Re(1)−Cl(3)	89.64(9)	88.75(10)
	P(3)−Re(1)−Cl(1)	89.17(9)	89.2(1)
	P(3)−Re(1)−Cl(2)	87.74(9)	88.8(1)
	P(3)−Re(1)−Cl(3)	173.53(9)	174.1(1)
	P(1)−Re(2)−Cl(4)	171.80(9)	172.06(9)
	P(1)−Re(2)−Cl(5)	85.86(9)	86.96(9)
	P(1)−Re(2)−Cl(6)	89.2(1)	89.2(1)
	P(2)−Re(2)−Cl(4)	90.07(9)	89.5(1)
	P(2)−Re(2)−Cl(5)	174.06(9)	173.43(9)
	P(2)−Re(2)−Cl(6)	87.62(9)	87.29(9)
	P(3)−Re(2)−Cl(4)	87.25(9)	87.7(1)
	P(3)−Re(2)−Cl(5)	89.56(9)	88.98(9)
	P(3)−Re(2)−Cl(6)	173.06(9)	172.9(1)
Cl−M−Cl	Cl(1)−Re(1)−Cl(2)	86.52(9)	85.9(1)
	Cl(1)−Re(1)−Cl(3)	87.22(9)	87.5(1)
	Cl(2)−Re(1)−Cl(3)	86.68(9)	86.0(1)
	Cl(4)−Re(2)−Cl(5)	86.97(9)	86.5(1)
	Cl(4)−Re(2)−Cl(6)	86.5(1)	86.1(1)
	Cl(5)−Re(2)−Cl(6)	87.1(1)	87.26(9)
(*μ*-P)−M−M	P(1)−Re(1)−Re(2)	59.37(7)	59.69(6)
	P(2)−Re(1)−Re(2)	59.36(7)	59.28(7)
	P(3)−Re(1)−Re(2)	59.38(6)	59.34(7)
	P(1)−Re(2)−Re(1)	59.31(7)	59.69(6)
	P(2)−Re(2)−Re(1)	59.25(6)	59.28(7)
	P(3)−Re(2)−Re(1)	59.37(6)	59.34(7)
Cl−M−M	Cl(1)−Re(1)−Re(2)	127.78(6)	127.21(7)
	Cl(2)−Re(1)−Re(2)	127.76(7)	129.35(7)
	Cl(3)−Re(1)−Re(2)	126.93(7)	126.62(7)
	Cl(4)−Re(2)−Re(1)	128.63(7)	128.16(7)
	Cl(5)−Re(2)−Re(1)	126.43(7)	127.22(7)
	Cl(6)−Re(2)−Re(1)	127.32(7)	127.54(7)
M−(*μ*-P)−M	Re(1)−P(1)−Re(2)	61.32(7)	61.26(6)
	Re(1)−P(2)−Re(2)	61.39(7)	61.33(7)
	Re(1)−P(3)−Re(2)	61.24(6)	61.51(7)

tronic complex **1** is fully diamagnetic with a rhenium−rhenium bond length of 2.4023(6) Å in (**1a**) and 2.4097(6) Å in (**1b**). This remarkable difference of ca. 0.3 Å in the metal−metal distances is clearly a consequence of replacing three bridging chlorides by phosphides. We recently discussed that phenomenon for dimolybdenum(III) FSBO systems.[16]

The $Re-P_{br}$ distances and the $Re-P_{br}-Re$ angles are 2.356(3) and 2.361(3) Å and 61.32(7) and 61.37(7)° (Table 2) for **1a** and **1b**, respectively. As we have already mentioned, the Re−Re distance in **1** now stands as the shortest M−M bond ever bridged by PEt_2^- groups, with the $Re-P_{br}-Re$ angles being the most acute. Prior to this work, this was observed[6c] in the trinuclear complex $[Co_2W(\mu\text{-}PEt_2)_3Cp(CO)_5]$, where one of the Co−W separations is 2.684 Å and the Co−P−W angle is 71.9°. However, for the whole range of *μ*-dialkylphosphido groups, the shortest M−M distance, 2.209 Å, was found[17] for two molybdenum atoms bridged by di-*tert*-butylphosphido groups with an $Mo-P_{br}-Mo$ angle of 53.95°. It is also worth noting that there is an unambiguous trans-effect of the phosphido ligands on the $Re-Cl_t$ bond lengths in **1**, which average to 2.430(3) Å (**1a**) and 2.438(3) Å (**1b**). The corresponding values in $[Re_2Cl_9]^-$, where all $Re-Cl_t$ bonds are trans to $Re-Cl_{br}$ ones, average to 2.283(5) Å,[10] which is about 0.15 Å shorter than those in **1**.

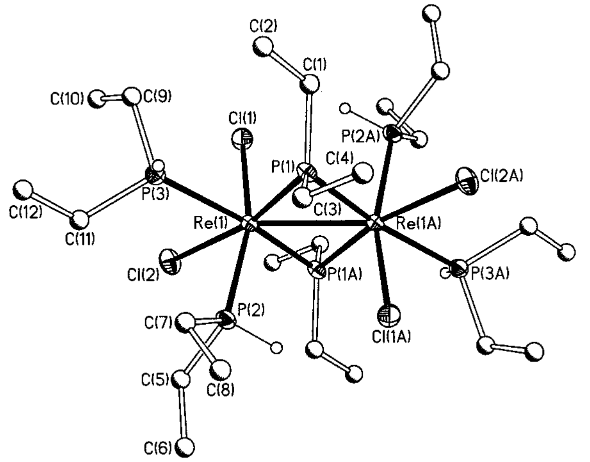

Figure 2. Perspective drawing of $Re_2(\mu\text{-}PEt_2)_2Cl_4(PEt_2H)_4$ (**2**). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon atoms are shown as spheres of arbitrary radius. Only hydrogen atoms on the PEt_2H ligands are depicted.

$Re_2(\mu\text{-}PEt_2)_2Cl_4(PEt_2H)_4$ (2). Polymorphic compounds **2a**,**b** crystallize in the monoclinic space group No. 14, where we have used the settings *P*2₁/*n* and *P*2₁/*c* for **2a** and **2b**, respectively, with two and four molecules in the unit cells. There are two independent centrosymmetric molecules present in the asymmetric unit of **2b**. Selected bond distances and angles for **2a** and **2b** are given in Table 3. Each molecule resides on an inversion center and consists of two rhenium atoms bridged by two phosphido groups. There are also two terminal phosphines and two chloride ligands on each metal center (Figure 2), which defines the structure as an edge-sharing bioctahedral dirhenium(III) complex. Even the $Re_2(\mu\text{-}P)_2Cl_4P_4$ core of the molecule has as its only symmetry element an inversion center. The arrangement of terminal phosphine ligands corresponds to the 1,2,5,6-isomer[18] of the edge-sharing complexes (Chart 2). This is the fifth type of $Re_2(\mu\text{-}Y)_2X_4L_4$ isomer (of a possible nine) which has been structurally characterized for dirhenium(III) ESBO complexes (Table 4). In addition, it is only the second Re_2 ESBO compound with monodentate phosphines. The other one described by us recently[1] as the 1,3,5,7-isomer of $Re_2(\mu\text{-}Cl)_2Cl_4(PMe_3)_4$ was found to be paramagnetic and to have no metal−metal bonding.

In complex **2** the rhenium−rhenium separation is 2.7551(6) Å (**2a**) indicative of the presence of the Re−Re bond. This is a bit larger than metal−metal distances for other known edge-

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[16] Cotton, F. A.; Dikarev, E. V.; Herrero, S. *Inorg. Chem.* **1998**, *37*, 5862−5868.

[17] Jones, R. A.; Lasch, J. G.; Norman, N. C.; Whittlesey, B. R.; Wright, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 6184.

[18] For the numbering scheme for edge-sharing complexes, see: Cotton, F. A.; Eglin, J. L.; James, C. A. *Inorg. Chem.* **1993**, *32*, 687.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 1,2,5,6-$Re_2(\mu\text{-}PEt_2)_2Cl_4(PEt_2H)_4$ (**2a** and **2b**)

	2a	**2b**		
Re(1)−Re(1A)	2.7551(6)	2.7577(8)	Re(2)−Re(2A)	2.7508(8)
Re(1)−P(1)	2.345(2)	2.353(2)	Re(2)−P(4A)	2.340(2)
Re(1)−P(1A)	2.327(2)	2.331(2)	Re(2)−P(4)	2.336(2)
Re(1)−P(2)	2.420(2)	2.405(2)	Re(2)−P(6)	2.409(2)
Re(1)−P(3)	2.487(2)	2.490(2)	Re(2)−P(5)	2.491(2)
Re(1)−Cl(1)	2.425(2)	2.418(2)	Re(2)−Cl(3)	2.445(2)
Re(1)−Cl(2)	2.487(2)	2.484(2)	Re(2)−Cl(4)	2.487(2)
P(2)−H(2)	1.23(7)	1.39(8)	P(5)−H(5)	1.37(8)
P(3)−H(3)	1.34(7)	1.28(8)	P(6)−H(6)	1.24(8)
P(1A)−Re(1)−P(1)	107.72(5)	107.87(6)	P(4)−Re(2)−P(4A)	107.93(6)
P(1)−Re(1)−P(2)	95.51(6)	93.21(8)	P(4A)−Re(2)−P(6)	95.39(7)
P(1A)−Re(1)−P(2)	93.99(6)	95.96(7)	P(4)−Re(2)−P(6)	93.33(7)
P(1)−Re(1)−P(3)	83.61(6)	83.86(7)	P(4A)−Re(2)−P(5)	85.02(7)
P(1A)−Re(1)−P(3)	168.47(6)	167.25(7)	P(4)−Re(2)−P(5)	167.01(7)
P(1)−Re(1)−Cl(1)	97.14(6)	100.44(8)	P(4A)−Re(2)−Cl(3)	96.70(8)
P(1A)−Re(1)−Cl(1)	92.19(6)	90.96(7)	P(4)−Re(2)−Cl(3)	93.10(7)
P(1)−Re(1)−Cl(2)	164.59(6)	165.70(7)	P(4A)−Re(2)−Cl(4)	165.73(7)
P(1A)−Re(1)−Cl(2)	87.69(6)	85.82(7)	P(4)−Re(2)−Cl(4)	86.33(7)
P(2)−Re(1)−P(3)	86.90(6)	88.17(7)	P(6)−Re(2)−P(5)	86.26(7)
P(2)−Re(1)−Cl(1)	163.52(6)	162.02(8)	P(6)−Re(2)−Cl(3)	163.85(8)
P(2)−Re(1)−Cl(2)	83.15(6)	80.98(8)	P(6)−Re(2)−Cl(4)	83.93(8)
Cl(1)−Re(1)−P(3)	84.06(6)	81.78(7)	Cl(3)−Re(2)−P(5)	84.16(7)
Cl(2)−Re(1)−P(3)	80.99(6)	82.91(7)	Cl(4)−Re(2)−P(5)	80.71(7)
Cl(1)−Re(1)−Cl(2)	81.85(6)	83.01(8)	Cl(3)−Re(2)−Cl(4)	81.71(8)
P(1)−Re(1)−Re(1A)	53.55(4)	53.56(5)	P(4A)−Re(2)−Re(2A)	53.89(5)
P(1A)−Re(1)−Re(1A)	54.17(4)	54.31(5)	P(4)−Re(2)−Re(2A)	54.04(5)
P(2)−Re(1)−Re(1A)	98.07(4)	97.79(5)	P(6)−Re(2)−Re(2A)	97.43(6)
P(3)−Re(1)−Re(1A)	137.11(4)	137.15(5)	P(5)−Re(2)−Re(2A)	138.89(5)
Cl(1)−Re(1)−Re(1A)	97.93(4)	99.72(5)	Cl(3)−Re(2)−Re(2A)	98.34(5)
Cl(2)−Re(1)−Re(1A)	141.86(4)	139.93(5)	Cl(4)−Re(2)−Re(2A)	140.37(5)
Re(1A)−P(1)−Re(1)	72.28(5)	72.13(6)	Re(2)−P(4)−Re(2A)	72.07(6)

Chart 2

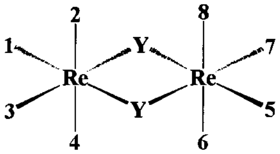

Table 4. Dirhenium(III) Edge-Sharing Complexes of the Type $Re_2(\mu\text{-}Y)_2X_4L_4$ (L = Neutral Donor)

compound	type	Re−Re, Å	ref
$Re_2(\mu\text{-}Cl)_2Cl_4(dppm)_2$	2,4,6,8	2.616(1)	19
$Re_2(\mu\text{-}Cl)_2Cl_3(OEt)(dppm)_2$	2,4,6,8	2.667(1)	19
$Re_2(\mu\text{-}SePh)_2Cl_4(dppm)_2$	2,4,6,8	2.656(1)	20
$Re_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)Cl_3H(dppm)_2$	2,4,6,8	2.592(1)	21
$Re_2(\mu\text{-}SH)(\mu\text{-}H)Br_4(dppm)_2$	2,4,6,8	2.457(1)	22
$Re_2(\mu\text{-}Cl)_2Cl_4(dmpm)_2$	2,4,6,8	2.5807(4)	23
$Re_2(\mu\text{-}Cl)_2Cl_4(dppe)_2$	1,3,5,7	3.809(1)	24
$Re_2(\mu\text{-}Cl)_2Cl_4(PMe_3)_4$	1,3,5,7	3.8476(4)	1
$Re_2(\mu\text{-}Cl)_2Cl_4(\text{tetraphos-1})^a$	1,2,7,8	2.625(1)	25
$Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2^b$	1,2,5,8	2.5925(9)	26
$Re_2(\mu\text{-}PEt_2)_2Cl_4(PEt_2H)_4$	1,2,5,6	2.7551(6)	this work

[a] tetraphos-1 = $Ph_2PCH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2$. [b] dto = 3,6-dithiaoctane.

sharing bioctahedral rhenium complexes of the type $Re_2(\mu\text{-}Y)_2X_4(LL)_2$ (LL = bidentate P or S-containing ligand) with the formal Re−Re bond order of 2 (Table 4). In addition, in complex **2** this bond is spanned by two diethylphosphido groups with about the same $Re-P_{br}$ distances (av 2.336(2) Å) as for **1**, but the $Re-P_{br}-Re$ angles are considerably larger (72.28(5)°). The terminal phosphine groups are located 2.420(2) and 2.487(2) Å (Table 3) away from the rhenium atom and the angle $P_t-Re-Pt$ is 86.90(6)°.

It also should be noted that there is strong hydrogen bonding in the structure of **2**. The hydrogen atoms on the axial phosphine groups (P(2) and P(2A), Figure 2) are directed toward the corresponding axial chlorine atoms (Cl(1A) and Cl(1), respectively) across the metal−metal bond. The P−H···Cl distances are 2.40 Å, and the P−H−Cl angle is 137°. That factor could make a significant contribution to the stability of **2** in the form of the rare 1,2,5,6-isomer.

Among all edge-sharing bioctahedral complexes of transition metals, the 1,2,5,6-isomers are relatively rare. All of them having metal−metal bonding (2.673−2.889 Å) and ranging from d^3-d^3 to d^6-d^6 electronic configurations, are listed in Table 5. Conversely, this is the most typical isomer for edge-sharing complexes of Bi^{III} and Sb^{III} which are, apparently, nonmetal−metal bonded, with monodentate[31] and bidentate phosphines,[32] and phosphine oxide ligands.[33] The same type of ligand distribution occurs rather often for the ESBO compounds of

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Table 5. 1,2,5,6-Isomers of the Complexes $M_2^{III}(\mu\text{-}Y)_2X_4L_4$ (L = Neutral Donor Ligand) with Metal−Metal Bonding

complex	electr. conf.	M−M, Å	∠L−M−L, deg	ref
$W_2(\mu\text{-}Cl)_2Cl_4(dmpe)_2$	d^3-d^3	2.6726(8)	77.5(1)	18
$MoW(\mu\text{-}Cl)_2Cl_4(dmpe)_2$	d^3-d^3	2.695(1)	77.1(2)	18
$Mo_2Cl_4[Et_2PCH_2CH_2P(Ph)CH_2P(Ph)]_2$	d^3-d^3	2.8312(3)	78.05(3)	25
$Mo_2(\mu\text{-}Cl)_2Cl_4(dto)_2$	d^3-d^3	2.735(2)	81.7(1)	27
$Re_2(\mu\text{-}PEt_2)Cl_4(PEt_2H)_4$	d^4-d^4	2.7551(6)	86.90(6)	this work[a]
$Os_2(\mu\text{-}PMePh)_2H_4(PMe_2Ph)_4$	d^5-d^5	2.889(1)	98.4(1)	28
$Ir_2(\mu\text{-}H)_2H_4(PMe_2Ph)_4$	d^6-d^6	2.739(1)	98.3(1)	29
$Ir_2(\mu\text{-}H)_2H_4(dfepe)_2$[b]	d^6-d^6	2.703(2)	85.1(2)	30

[a] Data for **2a**. [b] dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$.

V^{III},[34] V^{IV},[35] Ti^{III},[36] Ti^{IV},[37] and Nb^{IV}[38] with a metal-to-metal separation of more than 3.28 Å.

Two complexes from Table 5 could be considered to be close analogues of **2**. The first one is an osmium compound, $Os_2(\mu\text{-}PMePh)_2H_4(PMe_2Ph)_4$,[28] which has two phosphido groups bridging metal atoms and four terminal dimethylphenylphosphine ligands. The second one is a dimolybdenum complex with the diphosphine-phosphido ligand $Et_2PCH_2CH_2P(Ph)CH_2P(Ph)$[25] adopting a bis-chelating mode, with the phosphido P atom occupying the bridging position.

1,2,7,8-$Re_2Cl_4(PEt_2H)_4$ (3). Crystals of **3** conform to the monoclinic space group $P2_1/n$ with two molecules in the unit cell. The centrosymmetric molecule of **3** (Figure 3) consists of two *cis*-$ReCl_2P_2$ units brought together by a triple Re−Re bond of length 2.2533(8) Å in such a way that the core structure has virtual symmetry C_{2h}. This is the third member of the family of 1,2,7,8-$Re_2Cl_4(PR_3)_4$ isomers, of which the two other members were previously described by us for $PR_3 = PMe_3$[1] and PMe_2Ph.[2] All geometric characteristics of **3** (Table 6) are typical for this type of complex. The dirhenium molecule in **3** has a fully eclipsed conformation with the P−Re−Re−Cl torsion angles being 0.11(4) and 1.16(6)°. The P−Re−P angle for cis phosphine groups is 93.12(6)°. There is no indication of the influence on any structural parameters of P−H···Cl hydrogen bonding. In contrast to the PMe_3 and PMe_2Ph cases, where both *cis,cis*- and *trans,trans*-$Re_2Cl_4(PR_3)_4$ isomers are known,[1,2,12a,39] the 1,3,6,8-isomer of $Re_2Cl_4(PEt_2H)_4$ with trans location of diethylphosphine groups on both rhenium centers is still to be isolated. Our attempts to prepare it by reflux reaction of $[Re_2Cl_8]^{2-}$ with PEt_2H in alcohol has failed so far. It can be noted that not long ago we managed to synthesize and structurally characterize the 1,3,6,8-isomer for a quadruply bonded $Mo_2Cl_4(PEt_2H)_4$.[13]

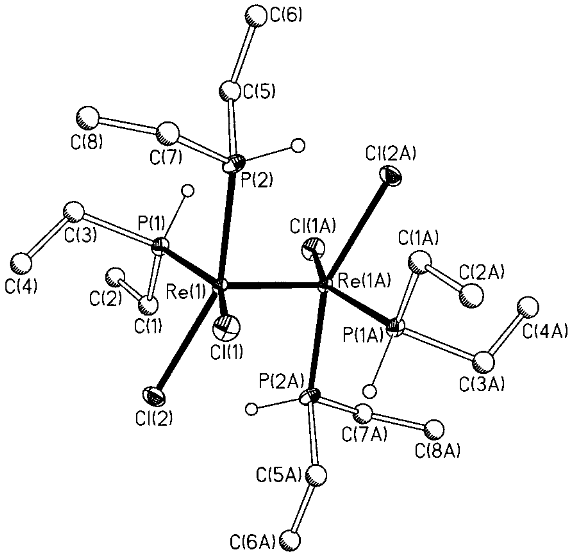

Figure 3. Perspective drawing of 1,2,7,8-$Re_2Cl_4(PEt_2H)_4$ (**3**). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and hydrogen atoms are shown as spheres of arbitrary radii.

Table 6. Averaged Bond Distances (Å) and Angles (deg) for 1,2,7,8-$Re_2Cl_4(PEt_2H)_4$ (**3**)

Re(1)−Re(1A)	2.2533(8)	Re(1)−Cl(2)	2.410(1)
Re(1)−P(1)	2.368(2)	P(1)−H(1)	1.40(6)
Re(1)−P(2)	2.364(1)	P(2)−H(2)	1.34(6)
Re(1)−Cl(1)	2.417(2)		
P(1)−Re(1)−P(2)	93.12(6)	Cl(1)−Re(1)−Cl(2)	82.79(5)
P(1)−Re(1)−Cl(1)	152.72(6)	Re(1A)−Re(1)−P(1)	94.29(4)
P(1)−Re(1)−Cl(2)	86.17(5)	Re(1A)−Re(1)−P(2)	93.94(3)
P(2)−Re(1)−Cl(1)	85.20(6)	Re(1A)−Re(1)−Cl(1)	112.99(4)
P(2)−Re(1)−Cl(2)	151.80(4)	Re(1A)−Re(1)−Cl(2)	114.24(4)

Spectroscopic Data. The phosphine-phosphido complexes are readily characterized by ^{31}P NMR spectroscopy. The face-sharing complex of rhenium(IV), $[Bu^n_4N][Re_2(\mu\text{-}PEt_2)_3Cl_6]$ (**1**), exhibits a singlet resonance in solution at the high-field value of 247 ppm, which is typical for μ-PEt_2 groups.[5,6] The rhenium(II) complex, 1,2,7,8-$Re_2Cl_4(PEt_2H)_4$ (**3**), with four equivalent coordinated diethylphosphine ligands, shows a singlet signal at 2.44 ppm in its $^{31}P\{^1H\}$ spectrum in accord with its symmetrical structure and the results for the PMe_3[1] and PMe_2Ph[2] analogues. The rhenium(III) complex, $Re_2(\mu\text{-}PEt_2)_2Cl_4(PEt_2H)_4$ (**2**), which has two types of coordinated phosphines as well as bridging phosphides, exhibits a complex, second-order spectrum with resonances ranging from 70 to −62 ppm.

The UV−vis spectrum of the $[Re_2(\mu\text{-}PEt_2)_3Cl_6]^-$ anion is dominated by a moderately intense absorption band at 29850 cm^{-1} and a more intense peak at 25840 cm^{-1}. We have no basis for determining which of these to assign to the $\delta \rightarrow \delta^*$ transition. Even interpretation of the spectrum of the related anion $[Re_2Cl_9]^-$ was somewhat challenging, because CT and δ

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$\rightarrow\delta^*$ transition were calculated to overlap.[10a] Careful inspection of the spectrum of **1** also reveals an additional weak and broad band in the low-energy region at 18940 cm^{-1}.

Complex **1** exhibits a reversible reduction at -0.69 V vs Ag/AgCl. This potential is very accessible, which means that the conversion to $[\mathrm{Re}_2(\mu\text{-PEt}_2)_3\mathrm{Cl}_6]^{2-}$ could be accomplished chemically as was done before for the isoelectronic $[\mathrm{Re}_2\mathrm{Cl}_9]^{1-/2-}$ couple.[10a,40] At the same time, we did not observe a second reduction potential for **1** analogous to that found for the $[\mathrm{Re}_2\mathrm{Cl}_9]^{2-/3-}$ couple. The oxidation of **1** at $+1.02$ V appears to be irreversible and may be accompanied by the destruction of the $[\mathrm{Re}_2(\mu\text{-PEt}_2)_3\mathrm{Cl}_6]^-$ core.

The 1,2,7,8-$\mathrm{Re}_2\mathrm{Cl}_4(\mathrm{PEt}_2\mathrm{H})_4$ (**3**) complex with the Re_2^{4+} core shows, as expected, two one-electron oxidations with half-wave potentials of $+0.03$ and 1.14 V vs Ag/AgCl, which is similar to the electrochemical behavior of the other two isomers of this type.[1,2]

Concluding Remarks

Three new dirhenium complexes have been isolated when reactions of $[\mathrm{Re}_2\mathrm{Cl}_8]^{2-}$ with $\mathrm{PEt}_2\mathrm{H}$ were performed in different solvents. A tentative explanation is presented here for the observed behavior of $\mathrm{PEt}_2\mathrm{H}$ under the conditions employed. We hope that further investigation of other secondary phosphines, such as PMePhH, and $\mathrm{PPh}_2\mathrm{H}$, $\mathrm{PCy}_2\mathrm{H}$, may be useful in understanding these transformations, and these studies are underway.

A major question arising when secondary phosphines are employed is how to control the deprotonation process and the formation of phosphido groups. It is evident that when diethylphosphine is substituting the relatively nonlabile chloride ligand, conditions are very favorable for deprotonation. This process can be retarded by using less polar solvents, employing only the amount of phosphine strictly required by stoichiometry, and moderate temperatures. In our work these mild conditions resulted in the coordination of $\mathrm{PEt}_2\mathrm{H}$ molecules as neutral terminal ligands, located cis to each other at $\mathrm{Re}^{\mathrm{III}}$ and $\mathrm{Re}^{\mathrm{II}}$ centers.

The formation of cis products in preference to, and indeed with the exclusion of, trans products is striking. Therefore, an interesting synthetic problem now is how to control not only deprotonation but also the formation of cis and trans isomers for $\mathrm{PEt}_2\mathrm{H}$. While the reaction of $[\mathrm{Re}_2\mathrm{Cl}_8]^{2-}$ with tertiary phosphines PR_3 under reflux conditions in polar solvents (alcohols, acetone) is a common method to produce 1,3,6,8-$\mathrm{Re}_2\mathrm{Cl}_4(\mathrm{PR}_3)_4$ complexes, a similar reaction with diethylphosphine has given only oily, unidentifiable products. It would be a synthetic challenge to prepare trans compounds and at the same time to avoid deprotonation of diethylphosphine. In addition, only two coordination modes (vide supra) of $\mathrm{PEt}_2\mathrm{H}$ have been seen in this work. The terminal coordination of PEt_2^- (Chart 1) is still to be found in rhenium chemistry.

Finally, we want to point out that the work reported here is still of an exploratory character. Based on what we report here and on many unpublished observations, we believe that further variations in reaction conditions, such as the use of higher temperatures, will lead to still other products and may also give further insight into reaction mechanisms. Thus, we are still actively pursuing research in this area.

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Supporting Information Available: Five X-ray files for **1a**,**b**, **2a**,**b**, and **3**, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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