Mixed Chloride Phosphine Complexes of Dirhenium Cores. 1. New Reactions and Unprecedented Structures Involving Trimethylphosphine

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Abstract: The unusual 1,2,7-isomer of $Re_2Cl_5(PMe_3)_3$ (**1**) has been used as a starting material to prepare previously unknown dirhenium complexes. One-electron reduction of **1** by cobaltocene followed by nonredox substitution of the resulting anionic species with PMe_3 led to the formation of a triply bonded 1,2,7,8-$Re_2Cl_4(PMe_3)_4$ (**2**). In the crystal structure of **2**, phosphine ligands on both metal centers exhibit a cis arrangement with a P−Re−P angle of 93.3° in contrast to the well-known type of 1,3,6,8-isomers with a trans arrangement of the monodentate phosphines connected to each metal atom. Complex **2** represents the first example of an isomer of this type in the large M_2X_4-$(PR_3)_4$ class of compounds (M = Re, Tc, W, Mo; X = Cl, Br, I; PR_3 = monodentate phosphine). The one-electron oxidation product of **1** cocrystallized with one molecule of tetrabutylammonium chloride afforded $Re_2Cl_6(PMe_3)_2$ (**3**), for which all previous synthetic attempts had failed. This quadruply bonded complex exhibits an unusual 3-fold disorder of the Re_2 unit with equal populations for all three orientations. We also report that when the "classic" reaction of octachlorodirhenate anion, $Re_2Cl_8^{2-}$, with trimethylphosphine is carried out in benzene at room temperature the reduction processes do not occur and the product is a novel paramagnetic complex, $Re_2Cl_6(PMe_3)_4$ (**4**), which does not have a metal−metal bond (the Re−Re separation is 3.8476(4) Å). Another interesting feature of compound **4** is that the PMe_3 ligands have a cis disposition at each rhenium center and are located in the same plane as the metal atoms and bridging chlorine ligands. For such a ligand arrangement the molecule of **4** is the only example of a nonmetal−metal-bonded dinuclear compound with monodentate phosphine ligands.
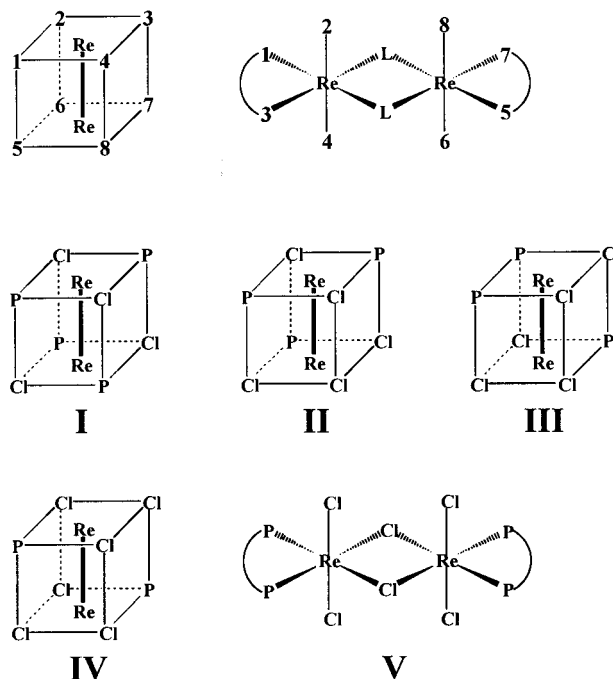
Introduction

Prior to this work, there were many compounds containing the dirhenium cores, Re_2^{4+}, Re_2^{5+}, and Re_2^{6+} complexed by a set of ligands comprised only of Cl^- ions and monophosphines (PR_3, PR_2Ar, and $PRAr_2$, where R is an alkyl and Ar an aryl group), but all of them fell within a limited range of stereochemistries. This is illustrated in Scheme 1, which shows several species that will be the subject of discussion in this paper.

For Re_2^{4+} all known[1a] $Re_2Cl_4(PR_3)_4$ compounds were of the type **I**, that is, they were the 1,3,6,8-$Re_2Cl_4(PR_3)_4$ isomers.[1b,2a] For Re_2^{5+} there were two types,[2a] namely the 1,3,6-Re_2Cl_5-$(PR_3)_3$ compounds **II** (R = Me, Et), and the 1,2,7-$Re_2Cl_5(PMe_3)_3$ isomer **III**. For Re_2^{6+}, there were only 1,7-$Re_2Cl_6(PR_3)_2$ (**IV**) compounds.[2b] There was no monophosphine analog to the remarkable edge-sharing bioctahedral compound,[3] 1,3,5,7-Re_2-$Cl_6(dppe)_2$ (**V**), reported by Walton[4] to have no Re−Re bond.

All structures of the types **I**−**IV** are consistent with the assumption that repulsion between ligands on the top and bottom (as drawn) decrease in the order $PR_3\cdots PR_3 > PR_3\cdots Cl \approx Cl\cdots Cl$, even for $PR_3 = PMe_3$, and of course for all phosphines with larger cone angles. It also needs to be noted that there is an overall eclipsed conformation in all of these species. In the

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(1) (a) Unless otherwise noted, we use the word "known" to mean that the structure has been obtained by X-ray crystallography. (b) Cotton, F. A.; Price, A. C.; Vidyasagar, K. *Inorg. Chem.* **1990,** *29,* 5143−5147. (The numbering scheme was first presented in this article.)

(2) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms,* 2nd ed.; Oxford University Press; Oxford, U.K., 1992; (a) Table 2.1.4, page 72; (b) Table 2.1.2, page 66.

(3) For the numbering scheme for edge-sharing complexes, see: Cotton, F. A.; Eglin, J. L.; James, C. A. *Inorg. Chem.* **1993,** *32,* 687−694.

(4) Jaecker, J. A; Robinson, W. R.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1975,** 698−701.

Scheme 1

1,7-$Re_2Cl_6(PR_3)_2$ case, this may be attributed to the presence of a full δ bond between the metal atoms. For the two Re_2-$Cl_5(PR_3)_3$ isomers, this may again be due to the existence of a δ bond of the order $^1/_2$. In $Re_2Cl_4(PR_3)_4$ molecules there is no δ bond present, but in the well-known 1,3,6,8-compounds, the overall eclipsed conformation has been attributed to the importance of minimizing $PR_3\cdots PR_3$ repulsions. It was assumed, prior to the discovery of 1,2,7-$Re_2Cl_5(PMe_3)_3$ (**1**), that

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a cis disposition of PR_3 ligands on either Re atom would also be disfavored sterically. While this may well be true for most monodentate PR_3 ligands, with the relatively small PMe_3 phosphine the cis arrangement is not ruled out. While one might suppose that $1,2,7$-$Re_2Cl_5(PMe_3)_3$ would be less stable than the $1,3,6$-isomer, no direct proof of this (e.g., thermal conversion of $1,2,7$ to $1,3,6$) has yet been obtained. However, the point remains moot because no $1,3,6$ to $1,2,7$ conversion has been obtained either.

The fact that the $Re_2Cl_5(PMe_3)_3$ compound could be obtained in two geometrical isomers caused us to suspect that there might be additional stereochemical variety to be found among other types of Re_2^{n+}-centered molecules. This has proved to be true, and we report here several interesting new compounds to illustrate the point. The lack of any homolog to the Walton compound also inspired us to look for a way to make one, and that too has been done and reported here. The approaches for the synthesis of previously unknown complexes could be classified as (I) the use of unusual starting materials in well-known reactions and (ii) new reaction conditions for "old" processes.

Experimental Section

General Procedures. All the syntheses and purifications were carried out under nitrogen or argon in standard Schlenkware. All solvents used were freshly distilled under N_2 from suitable drying reagents. Chemicals were purchased from the following commercial sources and used as received: PMe_3, Strem Chemicals; $Co(C_5H_5)_2$ and $NOBF_4$, Aldrich, Inc. Dichloromethane-d_2 was obtained from Cambridge Isotope Laboratories. General literature methods were used to prepare $[Bu^n_4N]_2[Re_2Cl_8]^5$ and $1,2,7$-$Re_2Cl_5(PMe_3)_3\cdot[Bu^n_4NCl]$.[6]

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. X-band ESR spectra of CH_2Cl_2 solutions were recorded at 10 K with a frequency of 9.4 GHz on a Bruker ESP300 spectrometer. The IR spectra were performed in the range $4000-400$ cm^{-1} on a Perkin-Elmer 16PC FT-IR spectrophotometer using KBr pellets. ^1H NMR spectra were obtained on a Varian XL-200 spectrometer operated at 200 MHz. Resonances were referenced internally to the residual proton impurity in the deuterated solvent. 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_3PO_4 as an external standard. The positive FAB/DIP (DIP = direct insertion probe) mass spectra were acquired using a VG Analytical 70S high resolution, double-focusing, sectored (EB) mass spectrometer. Samples for analysis were prepared either by dissolving the solid compound in a *m*-nitrobenzyl alcohol (NBA) matrix or mixing a solution of the compound in CH_2Cl_2 with an NBA matrix on the direct insertion probe tip. Elemental analyses were performed by Canadian Microanalytical Services, Ltd.

Synthetic Procedures. Preparation of $1,2,7,8$-$Re_2Cl_4(PMe_3)_4$ (2). Cobaltocene (0.024 g, 0.13 mmol) was added to the red-brown solution of $1,2,7$-$Re_2Cl_5(PMe_3)_3$ (0.1 g, 0.13 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred for 30 min until the color turned brown. PMe_3 (0.1 mL) was then added by syringe, and the mixture was stirred for about 1 h at room temperature, during which time its color changed to olive green. The solution was reduced in volume by half, and about 5 mL of benzene was added to precipitate cobaltocenium chloride. The solution was filtered, and the solvent was removed by reduced pressure to leave a dark green solid. After washing the solid with benzene, it

was dissolved in 5 mL of CH_2Cl_2 and layered with isomeric hexanes. In three days large block-shaped greenish-brown crystals of **2** were grown on the walls of the Schlenk tube. The yield was 0.078 g (74%). The crystals were stable in the air, but solutions slowly decomposed. ^1H NMR (CD_2Cl_2, 24 °C): δ 1.36 (s). ^{31}P $\{^1H\}$ NMR (CD_2Cl_2, 19 °C): δ -20.47 (s). CV (CH_2Cl_2, Ag/AgCl, 22 °C, V): $E_{1/2}$ (ox) (1) -0.16, $E_{1/2}$ (ox) (2) $+1.12$.

Preparation of $1,7$-$Re_2Cl_6(PMe_3)_2$ (3). Red crystals of $1,2,7$-$Re_2Cl_5(PMe_3)_3\cdot[Bu^n_4NCl]$ (0.116 g, 0.11 mmol) were dissolved in 10 mL of dichloromethane, and the solution was added by cannula to the Schlenk tube containing solid $NOBF_4$ (0.013 g, 0.11 mmol). A gas was released, and the color of the solution immediately turned green. The reaction mixture was stirred at room temperature for about 30 min and then a white precipitate ($Bu^n_4NBF_4$) was filtered off. After the solvent was removed, the resulting green solid was washed with hexanes (2×10 mL) and dissolved in 7 mL of CH_2Cl_2. After the solution was layered with hexanes, large green block- and cube-shaped crystals of **3** were obtained within 3 days. Yield: 0.065 g (80%). ^1H NMR (CD_2Cl_2, 24 °C): δ 1.26 (s). ^{31}P $\{^1H\}$ NMR (CD_2Cl_2, 19 °C): δ 3.05 (s). CV (CH_2Cl_2, Ag/AgCl, 22 °C, V): $E_{1/2}$ (red) (1) $+0.01$, $E_{1/2}$ (red) (2) -1.03. FAB/DIP (NBA, CH_2Cl_2, m/z): 703 ($[M - Cl]^+$), 625 ($[M - PMe_3 - Cl]^+$), 590 ($[M - PMe_3 - 2Cl]^+$), 554 ($[M - PMe_3 - 3Cl]^+$), 519 ($[M-PMe_3-4Cl]^+$).

Preparation of $1,3,5,7$-$Re_2Cl_6(PMe_3)_4$ (4). A suspension of $[Bu^n_4N]_2[Re_2Cl_8]$ (0.114 g, 0.1 mmol) in 15 mL of benzene was stirred for 6 h with an excess of PMe_3 (1 mL) at room temperature to give a pale-brown precipitate. The resulting brown solid was isolated by filtration and then washed with water and cold ethanol (partially soluble), to get rid of tetrabutylammonium chloride, and finally dried *in vacuo*. The yield was 0.031 g (35%). The red-brown single crystals of **4** were obtained in 2 days by layering dichloromethane solution with hexanes. In a few more days all crystals disappeared due to decomposition processes. The product that remained in the initial benzene solution was identified as the complex $1,2,7$-$Re_2Cl_5(PMe_3)_3\cdot[Bu^n_4$-NCl]^6 by X-ray. IR data (KBr pellet, ν (cm^{-1})): 1433 (m), 1426 (m), 1419 (m), 1309 (w), 1288 (s), 1281 (s), 1099 (s), 972 (s), 955 (s), 863 (m), 854 (m), 802 (m), 733 (s), 680 (m), 673 (s). FAB/DIP (NBA, CH_2Cl_2, m/z): 818 ($[M - 2Cl]^+$), 742 ($[M - PMe_3 - 2Cl]^+$, 707 ($[M - PMe_3 - 3Cl]^+$, 666 ($[M - 2PMe_3 - 2Cl]^+$, 631 ($[M - 2PMe_3 - 3Cl]^+$). Anal. Calcd for **4**, $Re_2Cl_6P_4C_{12}H_{36}$: Cl, 23.92; C,16.20; H, 4.08. Found: Cl, 23.36; C, 16.52; H, 4.11; N, < 0.10.

X-ray Crystallography. General Procedures. Single crystals of compounds **2**−**4** were obtained as described in the Synthetic Procedures section. X-ray diffraction study of **2** was performed with an Enraf-Nonius CAD-4S diffractometer and graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å) by using methods described previously.[7ab] A suitable single crystal was fastened to the end of a glass fiber with a thin layer of epoxy resin, and intensity data were collected at ambient temperature. 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 studies of **3** and **4** were carried out on an Enraf-Nonius FAST diffractometer with an area detector using Mo K_α radiation. Details for data collection have been fully described elsewhere.[7c] Each crystal was mounted on the tip of a quartz fiber with silicon grease and the setup was quickly placed in the cold N_2 stream (~ -60 °C) of the Model FR 558-S low-temperature controller. Fifty reflections were used in cell indexing and 240 reflections in cell refinement. Axial images were done to confirm the Laue group and cell dimensions. The data were corrected for Lorentz and polarization effects by the MADNES program.[8] Reflection profiles were fitted and

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(7) (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558−3562. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, 227−240. (c) Cotton, F. A.; Dikarev, E. V.; Feng, X. *Inorg. Chim. Acta* **1995**, *237*, 19−26.

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Table 1. Crystallographic Data for 1,2,7,8-Re$_2$Cl$_4$(PMe$_3$)$_4$ (**2**), 1,7-Re$_2$Cl$_6$(PMe$_3$)$_2$ (**3**), and 1,3,5,7-Re$_2$Cl$_6$(PMe$_3$)$_4$ (**4**)

	2	**3**	**4**
formula	Re$_2$Cl$_4$P$_4$C$_{12}$H$_{36}$	Re$_2$Cl$_6$P$_2$C$_6$H$_{18}$	Re$_2$Cl$_6$P$_4$C$_{12}$H$_{36}$
fw (g mol^{-1})	818.49	737.24	889.39
crystal system	monoclinic	cubic	orthorhombic
space group	$P2_1/n$ (No. 14)	$Pa\bar{3}$ (no. 205)	$Pbca$ (no. 61)
a (Å)	9.101(2)	12.3336(9)	15.627(2)
b (Å)	14.526(3)		10.872(1)
c (Å)	9.3519(9)		16.462(2)
β (deg)	91.24(1)		
V (Å^3)	1236.0(4)	1876.2(2)	2796.8(6)
Z	2	4	4
ρ_{calc} (g cm^{-3})	2.199	2.610	2.112
μ (mm^{-1})	10.471	13.894	9.449
data/observed^a/params.	2169/1779/137	411/410/44	2492/2282/181
R1,^{b} wR2^c [$I > 2\sigma(I)$]	0.038 0.097	0.024 0.047	0.026 0.059
R1,^{b} wR2^c (all data)	0.047 0.104	0.024 0.047	0.031 0.073
GOF^d	1.081	1.240	1.160

^{a} Observation criterion $I > 2\sigma(I)$. ^{b} $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$. ^{c} $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. ^{d} Based on F^2 for all data.

values of F^2 and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR, which uses a fitting algorithm developed by Kabsch.[9]

All calculations were done on a DEC Alpha running VMS. The coordinates of rhenium atoms for all of the structures were found in direct methods E-maps using the structure solution program SHELX-TL.[10] 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.[11]

Relevant crystallographic data for complexes **2**–**4** are summarized in Table 1, and selected bond distances and angles are given in Tables 2, 5, and 7. A full crystallographic report, including complete listings of atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, full list of bond distances and angles and hydrogen atomic coordinates (pages S1–S30) is available as Supporting Information.

1,2,7,8-Re$_2$Cl$_4$(PMe$_3$)$_4$ (2). The greenish-brown crystal selected was block-shaped with dimensions 0.35 × 0.28 × 0.23 mm. The data were collected in the 2θ range 5.18–49.96° for the whole sphere ($-10 \le h \le 10$, $-17 \le k \le 17$, $-11 \le l \le 11$) at ambient temperature. The crystal displayed a strong I-centered subcell, but by taking an oscillation photograph on [111] it was proved to have a P-lattice. Systematic extinctions uniquely determined the space group as $P2_1/n$ (no. 14). All absences were double checked by manual scans. After refining the position of the Re atom, the Fourier map revealed the positions of eight half-occupied chlorine and phosphorus sites about the metal atom, i.e., two sets of ligands with the second set slightly rotated from the first one (corresponding angles LReL′ ranged from 9.1 to 18.4°). A lowering of symmetry did not change the picture. Four crystals, each from a different synthesis, were used for X-ray experiments, and each one showed the same ligand distribution on the metal center. After least-squares refinement of Re, Cl and P atoms, 12 independent carbon ($^1/_2$ occupancy) atoms were located in a difference map. A second orientation of the Re-Re unit was located and refined at a site occupancy factor 0.025(2). Anisotropic displacement parameters were used for all atoms except C and H. Hydrogen atoms were included in the structure factor calculations at idealized positions and were allowed to ride on the corresponding carbon atoms. A final difference electron density map revealed two residual peaks >0.60 e Å^{-3}, both located in the vicinity of the Re atom.

Some further comment is required about the above-mentioned unusual disorder of chlorine and phosphine sites in this complex. It could be caused by either crystal twinning or statistical distribution of molecules in the crystal structure. In either case two models can be suggested for molecular structure of **2**. One of these assumes that all molecules are the same and noncentrosymmetric (Scheme 2a). In this

Scheme 2

a   **b**
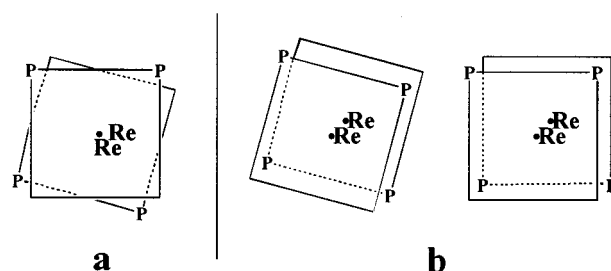
case we have a slightly twisted structure, with the torsion angles P−Re−Re−Cl ranging from 6.9 to 13.7°. The second model (Scheme 2b) is based on the assumption that all molecules are centrosymmetric and eclipsed, but that they are packed in a structure in two different ways. We have results on a similar compound, 1,2,7,8-Re$_2$Cl$_4$(PMe$_3$)$_3$-(PEt$_2$H),[13] which support the former model.
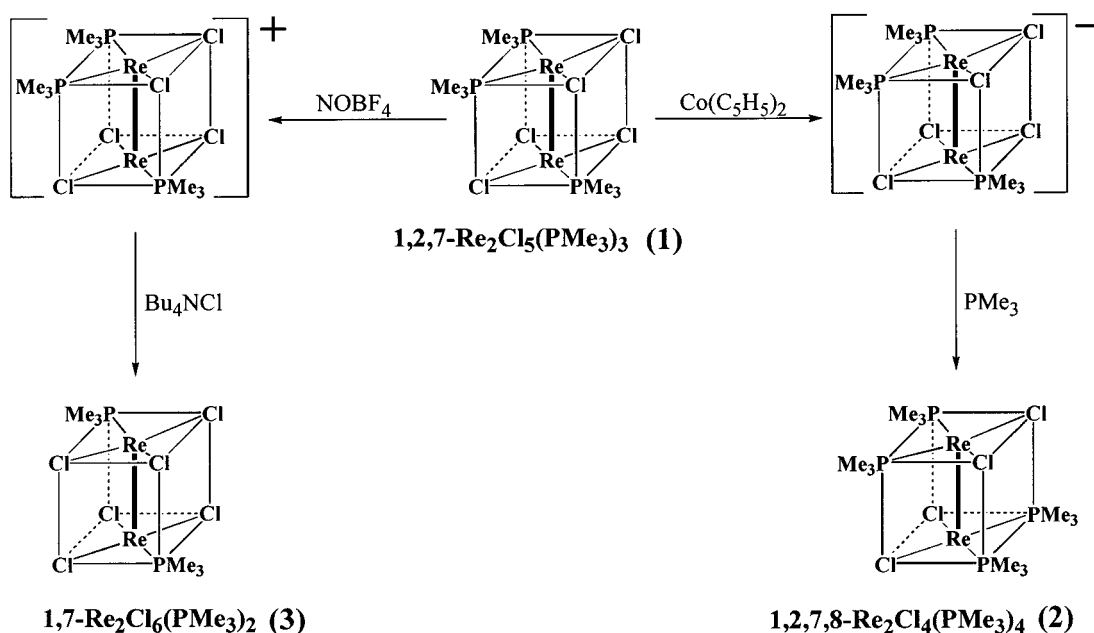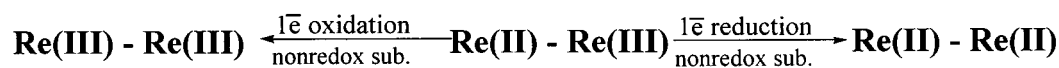
1,7-Re$_2$Cl$_6$(PMe$_3$)$_2$ (3). A dark-green block of size 0.25 × 0.25 × 0.20 mm was used for diffraction studies. Data collection was carried out in the range 5.72 ≤ 2θ ≤ 44.94° at −60 °C. The crystal was shown to belong to the primitive cubic system, and the analysis of statistics and systematic absences unambiguously assigned the space group as $Pa\bar{3}$. The rhenium, chlorine, and phosphorus atoms were located by direct methods. The rhenium atoms were found to reside on the general position (24d) and then form four octahedra centered at $\bar{3}$ positions (0 0 0, 4b). It was immediately recognized that each of the rhenium positions is actually occupied by $^1/_3$ Re because of 3-fold disorder. The phosphorus atom was found to be on the 3-fold axis (special position 8c). All atoms, except hydrogen, were refined anisotropically. Hydrogen atoms were taken as the three highest peaks on a Fourier map, and were refined. The final difference map was essentially featureless; the largest peak was 0.53 e Å^{-3}. Most of the Re$_2$Cl$_6$(PMe$_3$)$_2$ crystals grown in this reaction belong to the monoclinic system (space group $P2_1/c$ (no. 14), $a = 11.669(3)$, $b = 12.426(3)$, $c = 12.788(2)$ Å, $\beta = 92.09(2)°$, $V = 1853.0(7)$ Å^3, $Z = 4$). They were all twins, and we are not reporting the crystal structure here because of poor refinement (R = 0.0768). The monoclinic distortion of cubic space group is due to 2-fold disorder, with the primary orientations of Re$_2$ units 99.2 and 89.8% for two independent molecules.

1,3,5,7-Re$_2$Cl$_6$(PMe$_3$)$_4$ (4). A well-formed red-brown block with dimensions 0.18 × 0.08 × 0.08 mm was mounted for intensity measurements. Data were collected at −60 °C in the range 4.94 ≤ 2θ ≤ 50.30°. Laue symmetry *mmm* was displayed by axial photographs. The systematic extinctions uniquely determined the space group as $Pbca$ (no. 61). All the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms of the trimethylphosphine groups were then found in a difference Fourier map and also refined.

(9) (a) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21*, 67−71; (b) **1988**, *21*, 916−924.

(10) SHELXTL V.5, Siemens Industrial Automation Inc., Madison, WI, 1994.

(11) Sheldrick, G. M. In *Crystallographic Computing 6*; Flack, H. D., Parkanyi, L., Simon, K., Eds.; Oxford University Press: Oxford, U.K., 1993; pp 111−122.

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(13) Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. To be published.

Scheme 3

$$\text{Re(III) - Re(III)} \xleftarrow[\text{nonredox sub.}]{1\bar{e} \text{ oxidation}} \text{Re(II) - Re(III)} \xrightarrow[\text{nonredox sub.}]{1\bar{e} \text{ reduction}} \text{Re(II) - Re(II)}$$

1,2,7-Re$_2$Cl$_5$(PMe$_3$)$_3$ (1)

1,7-Re$_2$Cl$_6$(PMe$_3$)$_2$ (3)

1,2,7,8-Re$_2$Cl$_4$(PMe$_3$)$_4$ (2)

The only large peak in the final difference map was 1.09 e Å^{-3}, lying 1.363 Å from the Re atom.

Results and Discussion

Chemical Aspects. 1,2,7,8-Re$_2$Cl$_4$(PMe$_3$)$_4$ (2). The paramagnetic isomer 1,2,7-Re$_2$Cl$_5$(PMe$_3$)$_3$ (**1**) was first observed[1] in 1990 in the oxidation reaction of the Re^{II}–Re^{II} compound 1,3,6,8-Re$_2$Cl$_4$(PMe$_3$)$_4$. The structure of **1** was, and has remained until now, unique, as it was the only complex known with two monodentate phosphine ligands cis to each other on one rhenium center. More recently a quantitative method to produce (**1**)·[Bu$^n_4$NCl] by the reduction of Re^{III}–Re^{III} complexes has been reported.[6] This has allowed us to begin using **1** as a starting material in synthesis, and we believe this could provide routes to many unusual and unknown dirhenium complexes. In addition, complex **1** is known to exhibit very accessible redox chemistry ($E_{1/2}$ (red) = -0.48 V, $E_{1/2}$ (ox) = $+0.68$ V).[1,6] Thus, one-electron reduction and one-electron oxidation of **1** followed by nonredox substitution with trimethylphosphine or chlorine ligands, respectively, have been studied in this work (Scheme 3).

As a forerunner to our work the one-electron reduction of Re$_2^{5+}$ complexes was accomplished chemically a long time ago[12] via a one-electron transfer reaction with cobaltocene. In this case, the 1,3,6-isomer of Re$_2$Cl$_5$(PMePh$_2$)$_3$ was used, and the reaction of the reduced complex [(C$_5$H$_5$)$_2$Co][1,3,6-Re$_2$Cl$_5$-(PMePh$_2$)$_3$] with 1 equiv of PMePh$_2$ yielded the well-known 1,3,6,8-Re$_2$Cl$_4$(PMePh$_2$)$_4$ isomer, through the loss of chloride ion and the substitution by a phosphine ligand.

In this work (Scheme 3) the one-electron reduction of 1,2,7-Re$_2$Cl$_5$(PMe$_3$)$_3$ by cobaltocene in dichloromethane solution followed by nonredox substitution of Cl$^-$ in the resulting anionic species [1,2,7-Re$_2$Cl$_5$(PMe$_3$)$_3$]$^-$ with PMe$_3$ led to the formation of 1,2,7,8-Re$_2$Cl$_4$(PMe$_3$)$_4$, since substitution at any other position is unfavorable for steric reasons (PMe$_3$···PMe$_3$ contacts). It

should be noted that the presence of Cl$^-$ anions (i.e., Bu$^n_4$NCl) in the starting material drastically lowered the yield of the reaction. The intermediate anion and even the 1,3,6,8-Re$_2$Cl$_4$-(PMe$_3$)$_4$ isomer[13] could be identified in reaction products in this case.

It is worth mentioning that 1,2,7-Re$_2$Cl$_5$(PMe$_3$)$_3$ can be reduced by PMe$_3$ under refluxing conditions to give Re^{II}–Re^{II} complexes. However, the products in this case are those with *trans*-phosphines: [1,3,6-Re$_2$Cl$_5$(PMe$_3$)$_3$]$^-$ and 1,3,6,8-Re$_2$Cl$_4$-(PMe$_3$)$_4$. Thus we have the opportunity for stereochemical control of the reaction (that is, preserving a cis arrangement) at ambient (or low) temperature only.

1,7-Re$_2$Cl$_6$(PMe$_3$)$_2$ (3). Complexes of the Re$_2$Cl$_6$(PR$_3$)$_2$ stoichiometry are well-known for almost all monodentate phosphines except PMe$_3$.[2b] They can be easily produced by the reaction of octachlorodirhenium anion with phosphines under mild reaction conditions and in the presence of HCl which prevents any further reaction. Previous attempts to prepare Re$_2$-Cl$_6$(PMe$_3$)$_2$ in a similar way have failed.[1,6] An oxidation of Re$_2$Cl$_4$(PMe$_3$)$_4$ with 2 equiv of chlorine (or PhI·Cl$_2$) stops at the stage of Re^{II}–Re^{III} species formation.[1] The reaction of [Re$_2$Cl$_8$]$^{2-}$ with PMe$_3$ in acetone or alcohols affords a reduction product **1** even at room temperature and in the presence of HCl,[6] while this reaction in benzene does not stop at the Re$_2$Cl$_6$(PMe$_3$)$_2$ stage but continues to give edge-sharing complex Re$_2$-Cl$_6$(PMe$_3$)$_4$, as we shall explain below.

The oxidation of Re$_2$Cl$_5$(PR$_3$)$_3$ to [Re$_2$Cl$_5$(PR$_3$)$_3$]$^+$ by nitrosonium hexafluorophosphate was accomplished before[12] with R$_3$ = MePh$_2$. Addition of Cl$^-$ ion to the solution of the oxidized complex then leads to the formation of Re$_2$Cl$_6$(PMePh$_2$)$_2$, as was monitored by cyclic voltammetry.

We have carried out the one-electron oxidation of complex **1** in the presence of precisely 1 mol equiv of tetrabutylammonium chloride with which it cocrystallizes, to obtain the desired 1,7-Re$_2$Cl$_6$(PMe$_3$)$_2$ compound (Scheme 3). This is a good

Scheme 4
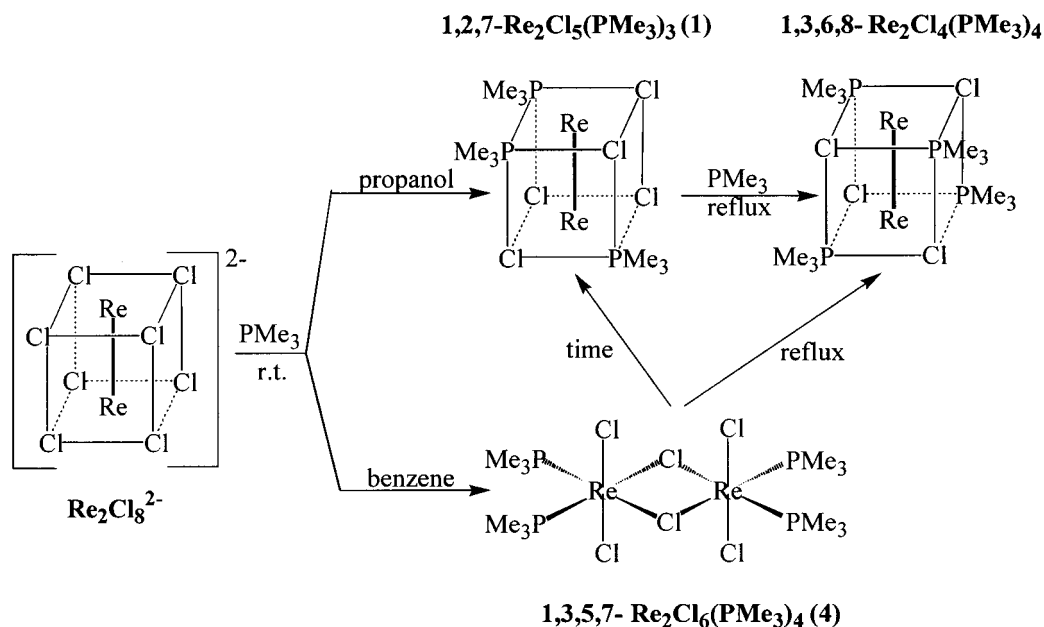
example of a "self-regulated" chemical process because the chloride source needed for the nonredox ligand substitution step is already present in the crystalline starting material in exactly the required proportion, 1:1. An equimolar amount of chloride substituent is absolutely critical for the desired process, as the use of an excess of Bu^n_4NCl results in other products, such as $[Re_2Cl_7(PMe_3)]^-$ and even $[Re_2Cl_8]^{2-}$.[13]

1,3,5,7-$Re_2Cl_6(PMe_3)_4$ (4). The only previously known example of the 1,3,5,7-$Re_2Cl_6P_4$ core type complex was isolated in 1975 by Walton[4] from a reaction of the bidentate phosphine 1,2-bis(diphenylphosphino)ethane (dppe) and $Re_2Cl_8^{2-}$ in acetonitrile. We have now found that under properly chosen conditions (*vide infra*) the monodentate phosphine, PMe$_3$, gives a similar 1,3,5,7 paramagnetic dirhenium complex in which there is no metal−metal bond present.

The reaction of $Re_2Cl_8^{2-}$ with PMe$_3$ has in the past been studied using refluxing alcohols or acetone as solvents, whereby a reduction process occurred yielding 1,3,6,8-$Re_2Cl_4(PMe_3)_4$.[14,15] 1,2,7-$Re_2Cl_5(PMe_3)_3$·[Bu^n_4NCl] has also been obtained at room temperature[6] as the first reduction step (Scheme 4). We decided to reinvestigate this reaction using an inert, nonpolar solvent, benzene, with the hope of eliminating the reduction processes so as to obtain Re^{III}−Re^{III}-type products. As hoped, the change of solvent had a great influence on the reaction pathway, and a rhenium(III) complex of stoichiometry $Re_2Cl_6(PMe_3)_4$ (4) was precipitated from benzene. The side product that remained in benzene solution was characterized by X-ray crystallography as complex 1·[Bu^n_4NCl].[6] In addition to the correct choice of solvent, careful control of other reaction conditions is absolutely critical in this process. Prolonging the reaction time significantly decreases the yield of 4 and favors the reduced product. Under reflux conditions, the reaction led to a mixture of Re^{II} compounds, of which the main one was 1,3,6,8-$Re_2Cl_4(PMe_3)_4$, as in the case of other solvents used. The compound 4 is relatively stable in the solid state and can be separated from Bu^n_4NCl with water or cold ethanol. In dichloromethane solution at room temperature complex 4 decomposed within a few days; one of the decomposition products was identified as monomeric $ReCl_3(PMe_3)_3$.[13]

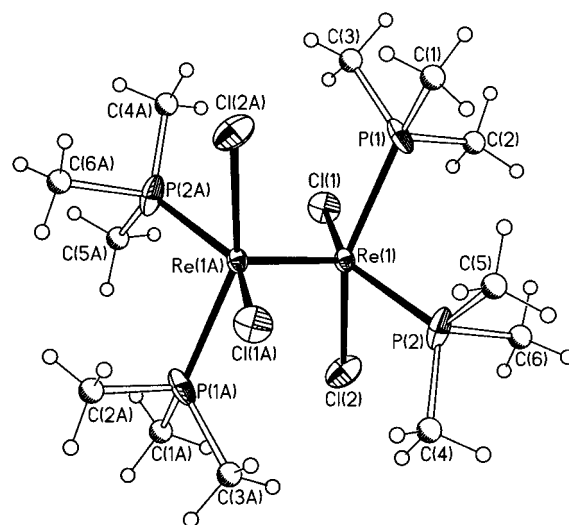(14) Ebner, J. R.; Walton, R. A. *Inorg. Chem.* **1975**, *14*, 1987−1992.
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Figure 1. Perspective drawing of 1,2,7,8-$Re_2Cl_4(PMe_3)_4$ (2). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and hydrogen atoms are shown as spheres of arbitrary radii.

Table 2. Averaged Bond Distances (Å) and Angles (deg) for 1,2,7,8-$Re_2Cl_4(PMe_3)_4$ (2)

Re(1)−Re(1A)	2.2414(8)	Re(1)−Cl(1)	2.414(7)
Re(1)−P(1)	2.362(8)	Re(1)−Cl(2)	2.405(10)
Re(1)−P(2)	2.384(7)		
P(1)−Re(1)−P(2)	93.2(3)	Cl(1)−Re(1)−Cl(2)	80.7(4)
P(1)−Re(1)−Cl(1)	146.0(4)	Re(1A)−Re(1)−P(1)	95.9(3)
P(1)−Re(1)−Cl(2)	84.4(4)	Re(1A)−Re(1)−P(2)	97.5(3)
P(2)−Re(1)−Cl(1)	83.4(3)	Re(1A)−Re(1)−Cl(1)	117.5(3)
P(2)−Re(1)−Cl(2)	146.9(4)	Re(1A)−Re(1)−Cl(2)	116.7(4)

Structural Details. 1,2,7,8-$Re_2Cl_4(PMe_3)_4$ (2). This compound crystallizes in the monoclinic space group $P2_1/n$ with two molecules in the unit cell. A perspective view of the molecular structure is shown in Figure 1, and selected bond lengths and angles are given in Table 2. The structure of 2 consists of a dirhenium unit with a metal−metal distance of 2.2414(8) Å, which is typical for Re^{II}−Re^{II} triple bonds. Phosphine ligands on the metal centers exhibit a cis arrangement, with an P−Re−P angle of 93.3(3)°. This is a bit smaller than the corresponding angle in the parent molecule 1 (96.60(7)°).[1]

Table 3. Key Molecular Dimensions (Å and deg) and Some Physical Characteristics for 1,2,7,8- and 1,3,6,8-Re$_2$Cl$_4$(PMe$_3$)$_4$ Isomers

	1,2,7,8-Re$_2$Cl$_4$(PMe$_3$)$_4$ (**2**)	1,3,6,8-Re$_2$Cl$_4$(PMe$_3$)$_4$
Re—Re	2.2414(8)	2.247(1)[a]
Re—P	2.373(7)	2.417(2)[a]
Re—Cl	2.410(8)	2.380(2)[a]
∠P—Re—P	92.3(2)	157.50(6)[a]
∠P—Re—Cl	83.9(3)	85.61(8)[a]
∠Re—Re—P	96.7(3)	101.18(6)[a]
∠Re—Re—Cl	117.1(3)	113.05(6)[a]
V(Re$_2$Cl$_4$(PMe$_3$)$_4$), Å^3	618.0(4)	643(1)[a]
^{1}H NMR, δ^c	1.36 (s)	1.29(s)[b]
^{31}P NMR, δ^d	−20.47 (s)	−21.51 (s)[b]
$E_{1/2}$ (ox) (1); (2)	−0.16; +1.12[e]	−0.23; +0.96[b,f]

[a] From ref 16. [b] From ref 15. [c] Recorded in CD$_2$Cl$_2$ at room temperature. [d] Recorded in CD$_2$Cl$_2$/CH$_2$Cl$_2$ at room temperature. [e] Volts vs Ag/AgCl in CH$_2$Cl$_2$−0.1 M TBAH at room temperature. [f] Volts vs Ag/AgCl in CH$_2$Cl$_2$−0.2 M TBAH at room temperature.
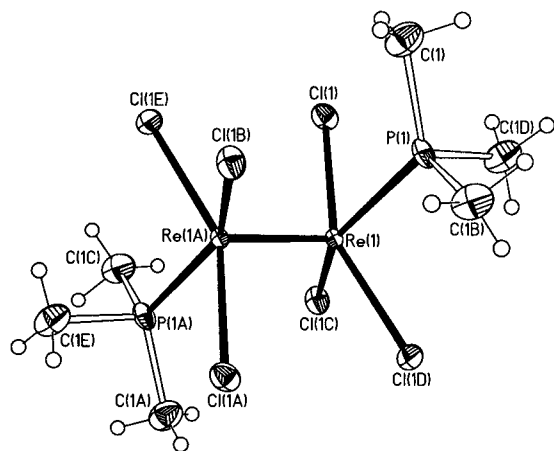
Figure 2. Perspective drawing of 1,7-Re$_2$Cl$_6$(PMe$_3$)$_2$ (**3**). Atoms are represented by thermal ellipsoids at the 40% probability level. Hydrogen atoms are shown as spheres of arbitrary radius. Only one orientation of the disordered Re$_2$ unit is depicted.

This contrasts to the well-known type of 1,3,6,8-isomers with a trans arrangement of monodentate phosphines on each metal center,[2a] and, in fact, complex **2** is the first example of a 1,2,7,8-isomer in the entire class of M$_2$X$_4$(PR$_3$)$_4$ compounds (M = Tc, Re, Mo, W; X = Cl, Br, I; PR$_3$ = monodentate phosphine).

Some averaged key dimensions and physical characteristics for complex **2** and for the corresponding 1,3,6,8-isomer are displayed in Table 3. A comparison of the Re−P and Re−Cl bond distances in both isomers reveals the presence of a strong trans influence. For the 1,3,6,8-isomer, where Re−P bonds and Re−Cl bonds are trans, respectively, to Re−P and Re−Cl bonds at each end of the molecule, the average Re−P and Re−Cl distances are 2.417(2) and 2.380(2) Å, respectively, whereas here they are 2.373(7) and 2.410(8) Å. This result is in accord with a previous description of this phenomenon for α-Re$_2$Cl$_4$(P-P)$_2$ type complexes. These compounds also have the 1,2,7,8-Re$_2$Cl$_4$P$_4$ core structure, but the four phosphorus atoms are supplied by two chelating diphosphines (P-P = dppp,[17] dmpe[18] and dppee[19]). The same effect was also observed for cis and trans ReCl$_2$(PMe$_3$)$_2$ configurations in 1,2,7- and 1,3,6-Re$_2$Cl$_5$-(PMe$_3$)$_3$.[1,6]

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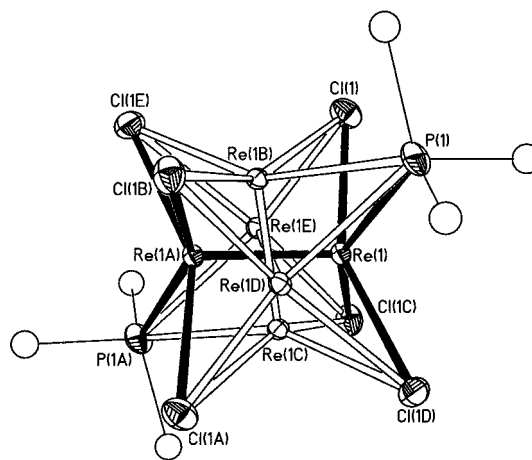
Figure 3. Drawing showing the three orientations of the Re$_2$ unit for the 1,7-Re$_2$Cl$_6$(PMe$_3$)$_2$ (**3**) molecule. Carbon atoms are shown as spheres of arbitrary radius.

Table 4. M$_2$L$_8$ Core Compounds with M$_2$ Units Equally Disordered in Three Directions

compound	M$_2$L$_8$ core	crystal system, space group	ref
Re$_2$Cl$_6$(PMe$_3$)$_2$	Re$_2$Cl$_6$P$_2$	cubic, $Pa\bar{3}$	this work
Re$_2$Cl$_6$(PEt$_3$)$_2$·C$_7$H$_8$	Re$_2$Cl$_6$P$_2$	rhombohedral, $R\bar{3}c$	20
Re$_2$Cl$_4$(PEt$_3$)$_4$	Re$_2$Cl$_4$P$_4$	cubic, $I\bar{4}3m$	21
Mo$_2$Cl$_4$(PEt$_3$)$_4$	Mo$_2$Cl$_4$P$_4$	cubic, $I\bar{4}3m$	21
Mo$_2$F$_4$(PEt$_3$)$_4$	Mo$_2$F$_4$P$_4$	cubic, $I\bar{4}3m$	22
Tc$_2$Cl$_4$(PEt$_3$)$_4$	Tc$_2$Cl$_4$P$_4$	cubic, $I\bar{4}3m$	23
[Bu$^n_4$N]$_2$[Re$_2$I$_8$]	Re$_2$I$_8$	rhombohedral, $R\bar{3}$	24
[(C$_5$Me$_5$)$_2$OsH][Os$_2$Br$_8$]	Os$_2$Br$_8$	hexagonal, $P\bar{3}$	25

Table 5. Selected Bond Distances (Å) and Angles (deg) for 1,7-Re$_2$Cl$_6$(PMe$_3$)$_2$ (**3**)

Re(1)−Re(1A)	2.208(1)	Re(1)−Cl(1C)	2.238(1)
Re(1)−P(1)	2.513(2)	Re(1)−Cl(1D)	2.402(1)
Re(1)−Cl(1)	2.396(1)		

P(1)−Re(1)−Cl(1)	84.31(3)	Cl(1C)−Re(1)−Cl(1D)	89.57(3)
P(1)−Re(1)−Cl(1C)	152.86(4)	Re(1A)−Re(1)−P(1)	94.57(3)
P(1)−Re(1)−Cl(1D)	84.18(3)	Re(1A)−Re(1)−Cl(1)	102.68(4)
Cl(1)−Re(1)−Cl(1C)	89.73(3)	Re(1A)−Re(1)−Cl(1C)	112.57(5)
Cl(1)−Re(1)−Cl(1D)	153.18(5)	Re(1A)−Re(1)−Cl(1D)	102.32(4)

There are some other significant differences between the two isomers of Re$_2$Cl$_4$(PMe$_3$)$_4$ (Table 3). Thus, the Re−Re−P angles are smaller in **2**, while Re−Re−Cl angles are larger; this may arise from molecular packing in the unit cell. It is interesting that the volume per molecule is considerably smaller (by 25 Å^3) for the 1,2,7,8-isomer, which indicates a significantly closer packing in the crystal structure of **2**. It must be noted that while the 1,3,6,8-Re$_2$Cl$_4$(PMe$_3$)$_4$ molecule shows no disorder of the dimetal unit[16] there is 0.975:0.025 ratio for the two possible orientations in the 1,2,7,8-compound. The ^{31}P-{^{1}H} NMR spectra show small upfield shifts for the cis-isomer, and the difference in $E_{1/2}$ (ox) potentials for these isomers agrees well with corresponding values for another pair of isomers: 1,2,7- and 1,3,6-Re$_2$Cl$_5$(PMe$_3$)$_3$.[1,6]

1,7-Re$_2$Cl$_6$(PMe$_3$)$_2$ (3). This compound forms crystals in the cubic space group $Pa\bar{3}$ with four molecules per unit cell. A crystal structure determination for **3** has shown the presence of a centrosymmetric, eclipsed molecule as represented in Figure 2. The Re−Re distance of 2.208(1) Å is consistent with the presence of a quadruple bond between the rhenium atoms. The arrangement of the trimethylphosphine ligands corresponds to the so-called 1,7-isomer—the only one known so far for compounds of M$_2$X$_6$(PR$_3$)$_2$ stoichiometry.[2b] The most interesting

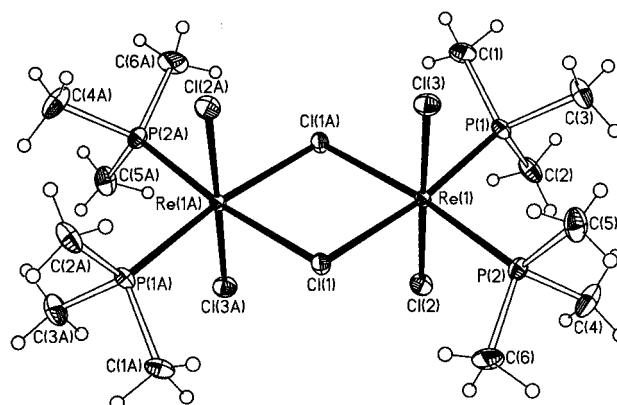**Table 6.** The Re−Cl Bond Lengths (Å) in ReCl₃P Parts of Molecules Re₂Cl₈₋ₓ(PR₃)ₓ (x = 1, 2, 3)

compound	disorder of Re₂ unit	Re−Cl$_{trans-P}$	Re−Cl$_{trans-Cl}$	Δ_{Re-Cl}[a]	ref
1,3,6-Re₂Cl₅(PMe₃)₃	1.00:0:0	2.373	2.330	+0.043	1
1,3,6 in 1,3,6/1,2,7-Re₂Cl₅(PMe₃)₃	1.00:0:0	2.386	2.330	+0.056	6
1,3,6-Re₂Cl₅(PMe₃)₃·¹/₂CH₂Cl₂	0.62:0.38:0	2.347	2.357	−0.010	6
1,2,7-Re₂Cl₅(PMe₃)₃	1.00:0:0	2.368	2.326	+0.042	1
1,2,7-Re₂Cl₅(PMe₃)₃·[Buⁿ₄NCl]	1.00:0:0	2.368	2.322	+0.046	6
1,2,7- in 1,3,6/1,2,7-Re₂Cl₅(PMe₃)₃	0.98:0.02:0	2.363	2.321	+0.042	6
1,3,6-Re₂Cl₅(PEt₃)₃	0.64:0.32:0.04	2.322	2.353	−0.031	1
Re₂Cl₆(PMe₃)₂ (cubic)	0.33:0.33:0.33	2.238	2.399	−0.161	this work
Re₂Cl₆(PMe₃)₂ (monoclinic)	0.99:0.01:0	2.353	2.296	+0.057	this work
	0.90:0.10:0	2.335	2.304	+0.031	
Re₂Cl₆(PEt₃)₂	1.00:0:0	2.350	2.300	+0.050	26
Re₂Cl₆(PEt₃)₂·C₇H₈	0.33:0.33:0.33	2.256	2.400	−0.144	21
Re₂Cl₆(PMePh₂)₂	1.00:0:0	2.337	2.315	+0.022	27
Re₂Cl₆(PMePh₂)₂·THF	0.97:0.03:0	2.326	2.314	+0.012	13
[Re₂Cl₇(PBuⁿ₃)](Ph₄As)	0.57:0.28:0.15	2.291	2.310	−0.019	28
[Re₂Cl₇(PBuⁿ₂Ph)](Ph₄As)	1.00:0:0	2.327	2.301	+0.026	29
	1.00:0:0	2.346	2.292	+0.054	
[Re₂Cl₇(PBuⁿPh₂)](Ph₄As)	1.00:0:0	2.339	2.298	+0.041	28

[a] $\Delta_{Re-Cl} = d(Re-Cl_{trans-P}) - d(Re-Cl_{trans-Cl})$.

structural feature is that the Re₂ units are equally disordered in three directions within a "cubic" cage of ligands (Figure 3). That type of disorder occurs rather rarely for M₂L₈ core compounds. All known examples to date are given in Table 4, including a triethylphosphine analog of the title compound with the same Re₂Cl₆P₂ core.

Most of the distances and angles in the molecule of **3** (Table 5) are in fair agreement with those in other known structures in the 1,7-Re₂Cl₆(PR₃)₂ class.[21,26,27] Again, however, we have found some very large discrepancies between the disordered and ordered structures. We expected to see a trans effect such that the Re−Cl bonds trans to Re−P bonds would be longer than cis ones. While it is fairly true for the ordered structures ($\Delta_{Re-Cl} \approx +0.06$ and +0.03 Å for two independent molecules), in the disordered structure of **3** we observe that effect in reverse, with trans Re−Cl bonds being 0.16 Å longer. That fact has been already mentioned for the two forms of Re₂Cl₆(PEt₃)₂[20,26] and was attributed to the influence of disorder on the apparent values of molecular dimensions. This point is supported by extensive statistics which became available recently (Table 6). It is clear that when we have one Re₂ orientation heavily predominant in a molecule (90−100%), we observe an unambiguous trans effect, while if significant disorder of dirhenium unit occurs, that effect appears to change its sign.

1,3,5,7-Re₂Cl₆(PMe₃)₄ (4). Crystals of **4** conform to the orthorhombic space group *Pbca* with four molecules per unit cell. The crystal structure of the paramagnetic compound **4** consists of a centrosymmetric chlorine-bridged edge-sharing

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Figure 4. Perspective drawing of 1,3,5,7-Re₂Cl₆(PMe₃)₄ (**4**). Atoms are represented by thermal ellipsoids at the 40% probability level. Hydrogen atoms are shown as spheres of arbitrary radius.

Table 7. Selected Bond Distances (Å) and Angles (deg) for 1,3,5,7-Re₂Cl₆(PMe₃)₄ (**4**)

Re(1)···Re(1A)	3.8476(4)	Re(1)−Cl(1A)	2.511(1)
Re(1)−P(1)	2.378(1)	Re(1)−Cl(2)	2.338(1)
Re(1)−P(2)	2.371(1)	Re(1)−Cl(3)	2.344(1)
Re(1)−Cl(1)	2.513(1)		
P(1)−Re(1)−P(2)	93.91(5)	P(2)−Re(1)−Cl(3)	92.04(5)
P(1)−Re(1)−Cl(1)	172.01(4)	Cl(1)−Re(1)−Cl(1A)	80.02(4)
P(1)−Re(1)−Cl(1A)	92.85(4)	Cl(1)−Re(1)−Cl(2)	90.56(4)
P(1)−Re(1)−Cl(2)	93.18(5)	Cl(1)−Re(1)−Cl(3)	89.65(4)
P(1)−Re(1)−Cl(3)	86.78(5)	Cl(1A)−Re(1)−Cl(2)	90.78(4)
P(2)−Re(1)−Cl(1)	93.36(4)	Cl(1A)−Re(1)−Cl(3)	90.62(4)
P(2)−Re(1)−Cl(1A)	172.86(4)	Cl(2)−Re(1)−Cl(3)	178.60(5)
P(2)−Re(1)−Cl(2)	86.57(5)	Re(1)−Cl(1)−Re(1A)	99.98(4)

bioctahedral dirhenium molecule (Figure 4). The Re−Re distance is 3.8476(4) Å indicating the absence of metal−metal bonding. The P−Re−P angle for the trimethylphosphine ligands is 93.91(5)°; they are located in the same plane as the metal centers and the bridging chlorine ligands. The angles Re−Cl$_b$−Re, Cl$_b$−Re−Cl$_b$, and Cl$_t$−Re−Cl$_t$ are 99.98(4), 80.02(4), and 178.60(5)°, respectively. All molecular dimensions (Table 7) are approximate those reported for Re₂Cl₆-(dppe)₂,[4] making **4** the first structural rhenium analog to Walton's compound. The only significant difference between the two structures is the P−Re−P angle which is much smaller in the diphosphine case (83.5(1)°)[4] because of the constraint of the 5-membered chelate ring.

Table 8. Characteristic Structural Parameters for the 1,3,5,7-$M_2Cl_6P_4$ Type of Complexes

complex	M−M	∠M−Cl$_b$−M	∠Cl$_b$−M−Cl$_b$	∠Cl$_t$−M−Cl$_t$	ref
		Monodentate Phosphines			
Re$_2$Cl$_6$(PMe$_3$)$_4$[a]	3.8476(4)	99.98(4)	80.02(4)	178.60(5)	this work
Zr$_2$Cl$_6$(PMe$_3$)$_4$	3.132(1)	75.97(7)	104.03(8)	162.05(9)	30a
Zr$_2$Cl$_6$(PEt$_3$)$_4$	3.169(1)	77.19(5)	102.81(5)	163.77(6)	31
Zr$_2$Cl$_6$(PBu$^n_3$)$_4$	3.182(1)	77.43(4)	102.57(5)	165.11(6)	32
Zr$_2$Cl$_6$(PMe$_2$Ph)$_4$	3.127(1)	75.74(7)	104.26(8)	162.1(1)	31
Hf$_2$Cl$_6$(PEt$_3$)$_4$	3.097(1)	75.38(5)	104.62(5)	165.75(6)	33
	3.118(1)[b]	75.78(4)	104.22(5)	165.33(6)	
Hf$_2$Cl$_6$(PMe$_2$Ph)$_4$	3.0886(3)	75.45(4)	104.55(5)	162.89(5)	34
		Bidentate Phosphines			
Re$_2$Cl$_6$(dppe)$_2$[a]	3.809(1)	99.5(1)	80.7(1)	178.0(1)	4
Ti$_2$Cl$_6$(dippe)$_2$[a]	3.438(2)	88.6(1)	91.4(1)	169.6(2)	35
Zr$_2$Cl$_6$(dppe)$_2$	3.099(2)	75.48(8)	104.52(8)	161.8(1)	31
	3.109(2)[b]	75.38(8)	104.62(8)	163.8(1)	
Hf$_2$Cl$_6$(dippe)$_2$	3.099(1)	76.0(1)	104.0(1)	166.5(1)	36
Mo$_2$Cl$_6$(dppe)$_2$	2.767(2)	70.1(1)	109.9(1)	164.3(2)	37
Mo$_2$Cl$_6$(dedppe)$_2$	2.785(3)	70.4(2)	109.6(2)	165.8(2)	38
MoWCl$_6$(dmpe)$_2$	2.7028(5)	67.69(5)	112.31(6)	164.03(6)	39
MoWCl$_6$(dppe)$_2$	2.7123(9)	68.58(8)	111.4(1)	163.9(1)	40
W$_2$Cl$_6$(dppe)$_2$	2.682(1)	67.87(9)	112.1(1)	164.2(1)	38
	2.680(1)[b]	67.90(9)	112.1(1)	163.0(1)	
Ta$_2$Cl$_6$(dmpe)$_2$	2.710(1)	66.88(4)	113.12(4)	163.08(5)	41
Ta$_2$Cl$_6$(depe)$_2$	2.724(1)	67.79(8)	112.21(9)	163.8(1)	42
	2.737(1)[b]	67.2(1)	111.8(2)	164.1(2)	
Nb$_2$Cl$_6$(dppe)$_2$	2.738(3)	67.7(1)	112.3(1)	164.6(1)	43
	2.721(2)[b]	67.7(1)	112.3(1)	163.1(1)	
Nb$_2$Cl$_6$(dppm)$_2$	2.696(1)	66.65(5)	113.35(5)	162.87(7)	44
Nb$_2$Cl$_6$(depe)$_2$	2.741(3)	68.0(2)	112.0(3)	164.1(3)	45

[a] No M−M bond. [b] Two crystallographically independent molecules.

Scheme 5

a   b
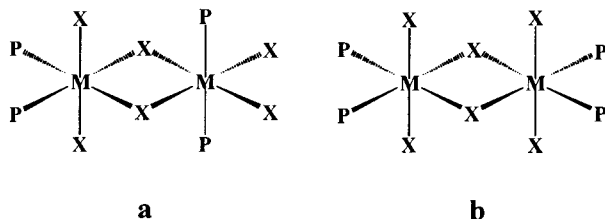
1,3,5,7-Re$_2$Cl$_6$(PMe$_3$)$_4$ is the first ever compound of the edge-sharing bioctahedral type for Re^{III} to contain monophosphine ligands. In the many other compounds with edge-sharing bioctahedral Re^{III}−Re^{III} units that have been reported, the phosphine ligands present are in the form of diphosphinomethanes which bridge adjacent axial positions (i.e., 2/6 and 4/8, Scheme 1). It is clearly interesting to contemplate the prospects for making more compounds with monophosphines, now that one has been shown to be obtainable. In fact, such other compounds can be made and we shall report on this in the near future.

Many other complexes of the type M$_2$X$_6$(PR$_3$)$_4$ (M^{III} = Ti, V, Ta, Cr, Mo, W, Ru, Rh; PR$_3$ = monodentate phosphine) are known[30] and most adopt the 1,3,6,8 configuration with two axial and two equatorial phosphine groups (Scheme 5a). The only other known examples of complexes containing a cis, coplanar arrangement of monodentate phosphines are 1,3,5,7-isomers (Scheme 5b) reported for Zr$_2$Cl$_6$(PR$_3$)$_4$ (R$_3$ = Me$_3$, Et$_3$, Bu$^n_3$, Me$_2$Ph) and for hafnium analogs Hf$_2$Cl$_6$(PR$_3$)$_4$ (R$_3$ = Et$_3$, Me$_2$-

Ph). The metal−metal separations were shown to be in the range 3.09−3.18 Å for the zirconium and hafnium compounds, which is consistent with the existence of single M^{III}−M^{III} bonds, as indicated by their diamagnetism. In addition, M−Cl$_b$−M angles of less than 90°, Cl$_b$−M−Cl$_b$ angles of more than 90°, and Cl$_t$−M−Cl$_t$ angles far from 180°, clearly indicate the presence of metal−metal bonding forces in the Zr and Hf complexes in contrast to the title compound **4**. Table 8 contains some characteristic structural parameters for all known complexes of the 1,3,5,7-M$_2$Cl$_6$P$_4$ type with both monodentate and bidentate phosphines.

Thus, complex **4** represents the first example of nonmetal−metal bonded 1,3,5,7-isomer with monodentate phosphine ligands. So far the cis arrangement of PR$_3$ groups in dirhenium compounds is known[1,6] only for PMe$_3$, although we shall soon describe another one. Other monodentate phosphines were found to afford different products under the same reaction

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conditions. It may be that failure to obtain homologs with other phosphines can be explained by steric difficulties occurring when two PR_3 ($R \neq Me$) ligands occupy cis positions about the rhenium center.

Concluding Remarks

Apart from the fact that the new compounds reported here are intrinsically interesting, this work as a whole shows that with a little synthetic ingenuity, entirely unanticipated compounds can be made. This synthetic creativity takes two forms: (i) the use of "old" reactions under new conditions (solvent, temperature), and (ii) the employment of novel starting materials. In the former class we have the preparation of 1,3,5,7-$Re_2Cl_6(PMe_3)_4$ by a route that had previously led only to reduction of the rhenium(III) in $Re_2Cl_8^{2-}$. In the latter class we use a starting material that had not previously been subjected to replacement of Cl^- by PR_3, or vice-versa, and achieve stereochemical control (Scheme 3).

The synthesis of 1,2,7,8-$Re_2Cl_4(PMe_3)_4$ (**2**) opens a previously unsuspected new class of multiply bonded compounds which may themselves serve as starting materials for the creation of more unusual molecules. An interesting question is: how wide may this class be for rhenium and for other metals such as Mo, W, and Tc taking into account the availability of starting materials and the steric difficulties when two phosphines occupy cis positions? Also, the possibility of a cis to trans conversion and its mechanism remain to be investigated.

Our choice of solvent for the preparation of 1,3,5,7-Re_2-$Cl_6(PMe_3)_4$ by reaction of $Re_2Cl_8^{2-}$ with PMe_3 was based on the assumption that the alcohols used in earlier studies could have been the actual reducing agents. However, with hindsight the problem seems more complex since even when benzene is used as a solvent some $Re^{II}-Re^{III}$ species were found to form along with the $Re_2Cl_6(PMe_3)_4$ (**4**). Nevertheless, it is reasonable to suggest that reduction processes are significantly slower in benzene, and that compound **4** might be an intermediate in the classical reaction pathway. The isolation of complex **4** may have occurred because it is insoluble in benzene, but soluble in acetone and alcohols. In any case, the actual reducing agent in the reactions between octachlorodirhenate and phosphines is still not identified.

Supporting Information Available: X-ray structural data for the three compounds listed in Table 1 including drawings, summaries of crystallographic parameters, atomic coordinates, anisotropic thermal parameters, bond distances and angles, and hydrogen atoms coordinates (30 pages). See any current masthead page for ordering and Internet access instructions.