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Mixed Chloride/Phosphine Complexes of the Dirhenium Core. 2. New Reactions Involving Dimethylphenylphosphine

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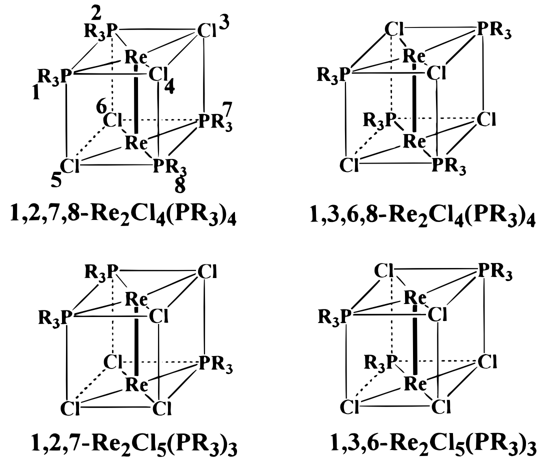
Two geometrical isomers of the composition $Re_2Cl_5(PMe_2Ph)_3$, namely 1,2,7 and 1,3,6, have been prepared. The unusual paramagnetic 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ (**1a**), the first analogue of the previously reported trimethylphosphine complex 1,2,7-$Re_2Cl_5(PMe_3)_3$, has been synthesized by carrying out the reaction of octachlorodirhenium anions with PMe_2Ph in benzene at room temperature. A different reaction product, 1,3,6-$Re_2Cl_5(PMe_2Ph)_3$ (**1b**), was obtained when $[Bu^n_4N]_2Re_2Cl_8$ was reacted with PMe_2Ph under the same conditions in acetonitrile. Electrochemical studies revealed that both **1a** and **1b**, as expected for the Re_2^{5+} core, are capable of undergoing a one-electron reduction and a one-electron oxidation to yield the respective Re_2^{4+} and Re_2^{6+} dinuclear complexes. Both processes have been accomplished chemically for the 1,2,7-isomer in the present work. One-electron reduction of **1a** by cobaltocene followed by nonredox substitution of a chloride ligand in the resulting anionic species by PMe_2Ph affords triply bonded 1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$ (**2**), only the second example of this rare stereochemistry with a cis-configuration of monodentate phosphines at both metal atoms in the large $M_2X_4(PR_3)_4$ class of compounds. One-electron oxidation of **1a** in the presence of a chloride source, Bu^n_4NCl, resulted in a quadruply bonded $Re_2Cl_6(PMe_2Ph)_2$ (**3**), completing the full series of $Re_2Cl_{8-x}(PMe_2Ph)_x$ ($x = 2, 3, 4$) compounds with Re_2^{n+} ($n = 6, 5, 4$) cores. The crystal structures of all complexes **1**−**3** have been investigated by X-ray diffraction. The crystallographic parameters for these structures are as follows: 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ (**1a**), triclinic space group $P\bar{1}$ with $a = 9.350(3)$ Å, $b = 11.102(1)$ Å, $c = 14.558(3)$ Å, $\alpha = 101.34(2)°$, $\beta = 92.81(2)°$, $\gamma = 90.80(2)°$, and $Z = 2$; 1,3,6-$Re_2Cl_5(PMe_2Ph)_3$ (**1b**), monoclinic space group $P2_1/c$ with $a = 11.202(4)$ Å, $b = 14.357(6)$ Å, $c = 19.509(5)$ Å, $\beta = 97.84(3)°$, and $Z = 4$; 1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$ (**2**), triclinic space group $P\bar{1}$ with $a = 11.847(4)$ Å, $b = 12.094(3)$ Å, $c = 13.056(5)$ Å, $\alpha = 76.111(8)°$, $\beta = 88.523(9)°$, $\gamma = 88.95(2)°$, and $Z = 2$; 1,7-$Re_2Cl_6(PMe_2Ph)_2$, (**3**), triclinic space group $P\bar{1}$ with $a = 9.209(1)$ Å, $b = 11.480(2)$ Å, $c = 13.389(2)$ Å, $\alpha = 81.74(2)°$, $\beta = 69.89(2)°$, $\gamma = 66.35(2)°$, and $Z = 2$. The Re−Re bond lengths in the Re_2^{4+} (**2**), Re_2^{5+} (**1a** and **1b**), and Re_2^{6+} (**3**) centered molecules (2.260(1), 2.2313(4), 2.219(1), and 2.214(1) Å) are consistent with bond orders of 3.0, 3.5, and 4.0, respectively.

Introduction

We recently[1] reported the preparation and crystal structure of a new type of stable geometrical isomer of $Re_2Cl_4(PMe_3)_4$, namely, the 1,2,7,8-isomer, with a cis-arrangement of trimethylphosphine ligands on each rhenium atom. Prior to that, compounds of the stoichiometry $Re_2Cl_4(PR_3)_4$ (R = monodentate phosphine) were known to exhibit only the 1,3,6,8-configuration (Chart 1) for a number of monodentate phosphines.[2] We have found a synthetic route to the 1,2,7,8-isomer which is based on the one-electron reduction of 1,2,7-$Re_2Cl_5(PMe_3)_3$ followed by nonredox substitution of one chloride ligand by a phosphine. The question of whether PMe_3 is the only phosphine capable of affording a cis-geometry at each rhenium center for steric reasons has been of special interest for us since then. The right choice of the starting material was also shown to be critical for synthesis of the 1,2,7,8-type isomer. Therefore, reactions of octachlorodirhenium anions, $Re_2Cl_8^{2-}$, with a number of other monodentate phosphines are being extensively studied in this research group.[3] We have attempted to find some other basic monodentate phosphines with small cone angles which can produce the 1,2,7-type of Re(II)−Re(III) compounds, since this is the first step toward the synthesis of the 1,2,7,8-isomers.

Chart 1



1,2,7,8-$Re_2Cl_4(PR_3)_4$ **1,3,6,8-$Re_2Cl_4(PR_3)_4$**

1,2,7-$Re_2Cl_5(PR_3)_3$ **1,3,6-$Re_2Cl_5(PR_3)_3$**

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(1) Part 1: Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 12541.

(2) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: New York, 1993.

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

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We have found that the use of benzene as a solvent instead of alcohols or acetone in "classical" reactions of $Re_2Cl_8^{2-}$ with PR_3 causes a large change in the reaction pathway. For example, the reaction of $Re_2Cl_8^{2-}$ with PMe_3 in benzene at room temperature resulted in the non-M−M-bonded edge-sharing complex of rhenium(III) $Re_2Cl_6(PMe_3)_4$[1] and in the mixed rhenium(II,III) complex 1,2,7-$Re_2Cl_5(PMe_3)_3 \cdot Bu^n{}_4NCl$ as a side product. In the present work, we report that the same reaction with PMe_2Ph in benzene results in 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ (**1a**) as the only product.

In contrast, when reaction of $Re_2Cl_8^{2-}$ with PMe_2Ph was performed in acetonitrile, both 1,2,7- and 1,3,6-$Re_2Cl_5(PMe_2Ph)_3$ (**1b**) were isolated. Thus, a change of solvent strongly influences the course of the reaction in this case.

Compound **1b** is of the well-known 1,3,6-geometrical type of the Re_2^{5+} core, while complex **1a** represents only the second example of the 1,2,7-stereochemistry for the $Re_2Cl_5(PR_3)_3$ stoichiometry (Chart 1) and provides us a stereochemically interesting starting material exhibiting very accessible potentials for one-electron reduction and one-electron oxidation reactions. The former results in a new dirhenium 1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$ (**2**) compound with a cis-arrangement of dimethylphenylphosphine ligands at each of rhenium centers.

As prior to this work only the series of [1,3,6,8-$Re_2Cl_4(PMe_2Ph)_4](PF_6)_n$ ($n = 0, 1, 2$) compounds were structurally characterized,[4] we decided to obtain the full set of Re_2^{n+} ($n = 4, 5, 6$) neutral molecules for the direct measurement of changes in the Re−Re bond lengths with changes in formal bond order. To this end, one-electron oxidation of **1a** was also accomplished, yielding 1,7-$Re_2Cl_6(PMe_2Ph)_2$ (**3**).

Synthetic methods and crystal structures and other characteristics of complexes **1**−**3** are reported here and compared to those for the corresponding trimethylphosphine analogues: 1,2,7- and 1,3,6-$Re_2Cl_5(PMe_3)_3$, 1,2,7,8-$Re_2Cl_4(PMe_3)_4$, and 1,7-$Re_2Cl_6(PMe_3)_2$.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere using standard Schlenk techniques. $[Bu^n{}_4N]_2Re_2Cl_8$, $NOBF_4$, $Bu^n{}_4NCl$, and $Co(C_5H_5)_2$ (Aldrich) and PMe_2Ph (Strem) were used as received. Dichloromethane-d_2 was obtained from Cambridge Isotope Laboratories. All solvents used were freshly distilled under N_2 from suitable drying agents.

Synthetic Procedures. 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ (1a). Method 1. To a suspension of 0.228 g (0.2 mmol) of $[Bu^n{}_4N]_2Re_2Cl_8$ in 15 mL of benzene was added 1 mL of PMe_2Ph. The mixture was stirred at room temperature for 3−4 days, resulting in a dark green precipitate. The solid was collected by filtration, washed with hexanes (2 × 10 mL), and dried under vacuum. It was then dissolved in 10 mL of CH_2Cl_2, and the dichloromethane solution was layered with hexanes. Greenish-brown block-shaped crystals of **1a** formed in a few days. Yield: 0.083 g (43%).

Method 2. To a suspension of 0.224 g (0.2 mmol) of $[Bu^n{}_4N]_2Re_2Cl_8$ in 15 mL of ethanol was added 0.6 mL of PMe_2Ph. The mixture was stirred at room temperature, and after 2 h the color of the solution turned dark green. Stirring was continued 2 h more, and the solvent was then removed under reduced pressure, leaving a dark, oily, green residue (contaminated with tetrabutylammonium chloride). This residue was thoroughly washed with hexanes and dried in a vacuum. Voltammetric measurements on a solution in dichloromethane indicated the presence of the 1,2,7-isomer only. A solution in 10 mL of CH_2Cl_2 was layered with 15 mL of hexanes; a few small crystals of **1a** appeared over a period of 2 weeks. Yield: 0.071 g (37%).

CV (CH_2Cl_2, 22 °C, V vs Ag/AgCl): $E_{1/2}(\text{red}) = -0.40$, $E_{1/2}(\text{ox}) = +0.75$. ESR ($CH_2Cl_2$, 100 K): centered at 2750 G, $g = 2.45$. FAB/DIP MS (NBA/CH_2Cl_2, m/z): 964 ($[M]^+$), 929 ($[M - Cl]^+$), 826 ($[M - PMe_2Ph]^+$), 791 ($[M - PMe_2Ph\text{-}Cl]^+$).

1,3,6-$Re_2Cl_5(PMe_2Ph)_3$ (1b). To a solution of 0.186 g (0.16 mmol) of $[Bu^n{}_4N]_2Re_2Cl_8$ in 10 mL of acetonitrile was added 0.5 mL of PMe_2Ph. The mixture became green in a few minutes. Stirring was continued for 1 h at room temperature without any further color change. The solvent was then removed under reduced pressure, leaving a dark-green solid, which was washed with hexanes (2 × 10 mL) and dried in a vacuum. Voltammetric measurements showed that the product was a mixture of the 1,3,6- and 1,2,7-isomers of $Re_2Cl_5(PMe_2Ph)_3$ in about a 1:2 ratio. Green block-shaped crystals of **1b** precipitated first from the acetone/dichloromethane solution layered with hexanes in a week. Yield: 0.101 g (64%).

CV (CH_2Cl_2, 22 °C, V vs Ag/AgCl): $E_{1/2}(\text{red}) = -0.67$, $E_{1/2}(\text{ox}) = +0.48$. ESR ($CH_2Cl_2$, 100 K): centered at 2743 G, $g = 2.45$. FAB/DIP MS (NBA/CH_2Cl_2, m/z): 964 ($[M]^+$), 929 ($[M - Cl]^+$), 826 ($[M - PMe_2Ph]^+$), 791 ($[M - PMe_2Ph\text{-}Cl]^+$), 718 ($[M - PMe_2Ph - 3Cl]^+$).

1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$ (2). Crystals of **1a**, 0.090 g (0.09 mmol), were mixed with 0.025 g (0.12 mmol) of $Co(C_5H_5)_2$, and 10 mL of CH_2Cl_2 was added. The mixture was stirred for 1 h at room temperature until the color turned dark green; 0.05 mL of PMe_2Ph was syringed into the suspension. Stirring was continued for about 1 h without noticeable change of color. The volume of the solution was then reduced by half, and 7 mL of benzene was added, causing precipitation of $Co(C_5H_5)_2Cl$. The mixture was filtered and the solvent was removed under reduced pressure, to leave a green residue. Yield: 0.074 g (78%). The solid was then dissolved in 10 mL of CH_2Cl_2, and the solution was layered with hexanes. A few small, green, block-shaped crystals were grown over a period of three weeks.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 19 °C): δ −20.67 (s). CV (CH_2Cl_2, 22 °C, V vs Ag/AgCl): $E_{1/2}(\text{ox})(1) = -0.17$, $E_{1/2}(\text{ox})(2) = +0.98$. FAB/DIP MS (NBA/$CH_2Cl_2$, m/z): 1067 ($[M]^+$), 929 ($[M - PMe_2Ph]^+$), 755 ($[M - 2PMe_2Ph - Cl]^+$).

1,7-$Re_2Cl_6(PMe_2Ph)_2$ (3). Crystals of $Re_2Cl_5(PMe_2Ph)_3$ (**1a**), 0.098 g (0.10 mmol), were mixed with 0.015 g (0.125 mmol) of $NOBF_4$ and 0.028 g (0.10 mmol) of $Bu^n{}_4NCl$, and 10 mL of CH_2Cl_2 was then added to the solids. The mixture was stirred for about 1 h at room temperature under reduced pressure. The solvent was then removed, to leave a green residue, which was washed with small portions of hexanes, pumped to dryness, and redissolved in 10 mL of CH_2Cl_2. Olive-green, plate-shaped crystals appeared in a few days upon layering of the dichloromethane solution with hexanes. Yield: 0.063 g (73%).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 19 °C): δ 0.47 (s). CV (CH_2Cl_2, 22 °C, V vs Ag/AgCl): $E_{1/2}(\text{red})(1) = +0.06$, $E_{1/2}(\text{red})(2) = -0.93$.

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 solutions 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 a Bioanalytical Systems Inc. electrochemical analyzer, model 100. The scan rate was 100 mV/s at a Pt disk electrode. $^{31}P\{^1H\}$ NMR spectra were obtained on a UNITY-plus 300 multinuclear spectrometer at 121.4 MHz. Resonances in $^{31}P\{^1H\}$ NMR data were referenced to the external standard 85% H_3PO_4 (0.00 ppm). X-band ESR spectra of dichloromethane glasses were recorded at 100 K with a frequency of 9.4 GHz on a Bruker ESR 300 spectrometer. The positive FAB/DIP mass spectra were acquired using a VG Analytical 70S high-resolution, double-focusing, sectored (EB) mass spectrometer. Samples for analyses were prepared by mixing a solution of each compound in CH_2Cl_2 with an NBA matrix on the direct insertion probe tip.

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

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(4) Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tomas, M.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 4950.

Table 1. Crystallographic Data for 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ (**1a**), 1,3,6-$Re_2Cl_5(PMe_2Ph)_3$ (**1b**), 1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$ (**2**), and 1,7-$Re_2Cl_6(PMe_2Ph)_2$ (**3**)

	1a	**1b**	**2**	**3**
formula	$Re_2Cl_5P_3C_{24}H_{33}$	$Re_2Cl_5P_3C_{24}H_{33}$	$Re_2Cl_4P_4C_{32}H_{44}$	$Re_2Cl_6P_2C_{16}H_{22}$
fw	964.06	964.06	1066.75	861.38
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No.14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	9.350(3)	11.202(4)	11.847(4)	9.209(1)
b, Å	11.102(1)	14.357(6)	12.094(3)	11.480(2)
c, Å	14.558(3)	19.509(5)	13.056(5)	13.389(2)
α, deg	101.34(2)	90.00	76.111(8)	81.74(2)
β, deg	92.81(2)	97.84(3)	88.523(9)	69.89(2)
γ, deg	90.80(2)	90.00	88.95(2)	66.35(2)
V, Å^3	1479.5(6)	3108(2)	1815(1)	1217.6(3)
Z	2	4	2	2
ρ_{calc}, g cm^{-3}	2.164	2.060	1.952	2.350
μ, mm^{-1}	8.803	8.380	7.156	10.724
radiation (λ, Å)	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
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.024, 0.061	0.057, 0.143	0.047, 0.117	0.050, 0.127
R1,[a] wR2[b] (all data)	0.029, 0.063	0.065, 0.153	0.055, 0.128	0.054, 0.132

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

monochromated Mo Kα radiation, Enraf-Nonius CAD-4S (**1a**) and Enraf-Nonius FAST (**1b**, **2** and **3**). Unit cell determination and data collection followed routine procedures and practices of this laboratory.[5] Oscillation photographs of principal axes were taken to confirm the Laue class and axial lengths. All data were corrected for Lorentz and polarization effects.

The structures were solved and refined using the SHELXTL direct methods[6] and the SHELXL-93 programs[7] on a DEC Alpha running VMS. In each model, hydrogen atoms were included at idealized positions for the structure factor calculations but were not refined. Details on data collection and structure refinement are reported in Table 1.

1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ (1a). A green block of dimensions 0.35 × 0.15 × 0.10 mm was selected for diffraction studies. The ω scan technique was used to scan data points. There was no significant decay of the crystal, as indicated by the intensity standards. An empirical absorption correction based on azimuthal scans of nine reflections with their ψ angles near 90° was applied. Choice of the centrosymmetric space group $P\bar{1}$ revealed the positions of the Re atoms, and successful refinement of the structure confirmed the choice. Anisotropic displacement parameters were assigned to all atoms, except hydrogen. Final least-squares refinement of 307 parameters converged with $R = 0.024$ (for 3683 reflections with $I > 2\sigma(I)$) and $R = 0.029$ (for all 4081 data). The largest peak in the final difference Fourier map had an electron density of 1.50 e/Å^3, lying 0.948 Å from the Re atom.

1,3,6-$Re_2Cl_5(PMe_2Ph)_3$ (1b). All crystals of **1b** tried for X-ray diffraction study were twinned or had some satellites attached. A dark green crystal with approximate dimensions 0.30 × 0.15 × 0.08 mm was selected. Indexing and refinement of 247 reflections with 18 < 2θ < 42° gave the unit cell parameters which were very close to those reported for the Tc analogue.[8] Systematic absences in the data uniquely determined the space group to be $P2_1/c$. The intensities were corrected for absorption anisotropy effects using a local adaptation of the program SORTAV.[9] The non-hydrogen atoms in the molecule were refined anisotropically. The final residuals were $R = 0.057$ (for 3490 reflections with $I > 2\sigma(I)$) and $R = 0.065$ (for all 4057 data and 307 parameters). A final difference Fourier map contained several large peaks lying less than 1.0 Å from the Re atoms.

1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$ (2). A small green crystal of dimensions 0.15 × 0.10 × 0.10 mm was mounted. Indexing based on 50 reflections in the range 14 < 2θ < 42° resulted in a triclinic cell, and cell parameters were further refined against 216 reflections. No absorption correction was made. Direct method solutions based on the space group $P\bar{1}$ readily afforded the atomic positions of the unique Re atoms corresponding to the two independent dirhenium units in a cell. No metal nor ligand disorder was detected. After anisotropic refinement of all non-hydrogen atoms, 379 parameters, the residuals were $R = 0.047$ (for 3943 reflections with $I > 2\sigma(I)$) and $R = 0.055$ (for all 4476 independent reflections). The only large peak in the final difference map was 2.83 e/Å^3, lying 1.22 Å from the Re(1) atom.

1,7-$Re_2Cl_6(PMe_2Ph)_2$ (3). A green plate of dimensions 0.18 × 0.15 × 0.05 mm was mounted. Indexing based on 221 reflections with 18 < 2θ < 42° gave a triclinic cell. Space group $P\bar{1}$ was chosen and confirmed by successful refinement. Direct methods provided the positions of two independent dinuclear molecules. Final anisotropic refinement of 235 parameters resulted in $R = 0.050$ (for 2550 reflections with $I > 2\sigma(I)$ and $R = 0.054$ (for all 2760 data). A final difference map revealed several small peaks associated with the rhenium atoms.

Results and Discussion

Chemical Aspects. Trimethylphosphine had been the only phosphine so far known to afford unprecedented 1,2,7-$Re_2Cl_5(PMe_3)_3$[10] and 1,2,7,8-$Re_2Cl_4(PMe_3)_4$[1] types of isomers with a cis-arrangement of phosphine ligands coordinated to one rhenium atom. As a part of our search for some other basic monodentate phosphines with small cone angles able to exhibit cis-type geometries at rhenium centers, we have selected PMe_2Ph, the close analogue of PMe_3.

In addition, we were interested in the use of solvents other than alcohols and acetone for studying the reactions of $Re_2Cl_8^{2-}$ with PR_3. Recently we observed[1] that 5−6 h of stirring the suspension containing $Re_2Cl_8^{2-}$ and PMe_3 in benzene results in the novel $Re_2Cl_6(PMe_3)_4$ complex without Re−Re bonding, which precipitated from the solution. The side product of this reaction, soluble in benzene, was found to be 1,2,7-$Re_2Cl_5(PMe_3)_3 \cdot Bu^n_4NCl$.

By carrying out the reaction of $Re_2Cl_8^{2-}$ with dimethylphenylphosphine in benzene at room temperature in this work, we isolated the paramagnetic 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ (**1a**) as the only product. In the case of PMe_2Ph, the transformation of $Re_2Cl_8^{2-}$ proceeds much more slowly than that with PMe_3.

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

(6) *SHELXTL V.5*; Siemens Industrial Automation Inc.: Madison, WI, 1994.

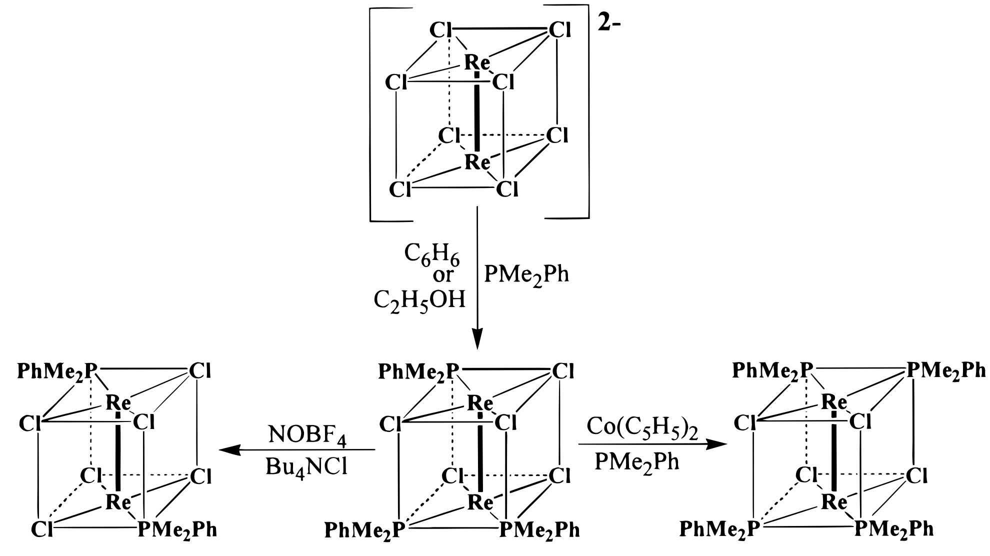
(7) Sheldrick, G. M. In *Crystallographic Computing 6*; Flack, H. D., Parkanyi, L., Simon, K., Eds.; Oxford University Press: Oxford, U.K., 1993; p 111.

(8) Cotton, F. A.; Haefner, S. C.; Sattelberger, A. P. *Inorg. Chem.* **1996**, *35*, 1831.

(9) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(10) Cotton, F. A.; Price, A. C.; Vidyasagar, K. *Inorg. Chem.* **1990**, *29*, 5143.

Scheme 1



1,7-$Re_2Cl_6(PMe_2Ph)_2$ **(3)** 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ **(1a)** 1,2,7,8- $Re_2Cl_4(PMe_2Ph)_4$ **(2)**

Interestingly, no dimethylphenylphosphine analogue of $Re_2Cl_6(PMe_3)_4$ has been seen in this work. Room-temperature reaction in benzene in the dimethylphenylphosphine case produces only 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$, which is not very soluble in benzene and is precipitated from the solution over a period of 1−2 days. A possible explanation could be based on the different solubilities in benzene of the trimethyl- and dimethylphenylphosphine products of the stoichiometry $Re_2Cl_6(PR_3)_4$. The latter might be an intermediate on the way to 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$, but because of its good solubility in benzene, it does not precipitate and is entirely converted to the insoluble Re_2^{5+} product. Thus, substitution of one methyl group by a phenyl ring in the phosphine proves to be critical in this case, only because of its effect on solubility. We do not see any reason for dimethylphenylphosphine to directly destabilize the $Re_2Cl_6(PR_3)_4$ type of structure.

Whatever may be the exact reasons, the reaction of $Re_2Cl_8^{2-}$ with PMe_2Ph in benzene provides a convenient synthetic route to **1a**, the second representative of the 1,2,7 type of stereochemistry for the Re_2^{5+} core. It is important that complex **1a** crystallizes in pure form, which makes it much easier to control the substitution of Cl^- by the PMe_2Ph in the following reduction process. This contrasts with the trimethylphosphine analogue of **1a**, where synthesis resulted in isolation of crystals with one molecule of tetrabutylammonium chloride per dirhenium unit, $Re_2Cl_5(PMe_3)_3 \cdot Bu^n_4NCl$.[11]

Prior to this work, the formation of the 1,3,6-isomer of $Re_2Cl_5(PMe_2Ph)_3$ was observed only by cyclic voltammetry in electrochemically oxidized solutions of 1,3,6,8-$Re_2Cl_4(PMe_2Ph)_4$, through the reaction $[Re_2Cl_4(PMe_2Ph)_4]^+ + Cl^- \rightarrow Re_2Cl_5(PMe_2Ph)_3 + PMe_2Ph$.[4] We have now found that, by performing the reaction of $Re_2Cl_8^{2-}$ with PMe_2Ph in acetonitrile at room temperature, we can isolate 1,3,6-$Re_2Cl_5(PMe_2Ph)_3$ as a mixture with 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$. This further confirms our observation[1] that a change of solvent has a great influence on the reaction of octachlorodirhenium anions with phosphine ligands. No interconversion between these two isomers, namely 1,3,6 and 1,2,7, has been seen in our experiments.

Compounds **1a** and **1b** appear stable in both solution and the solid state. However, when a Schlenk tube containing a dichloromethane solution of $Re_2Cl_5(PMe_2Ph)_3$ was inadvertently exposed to air, dark brown plate-shaped crystals of [1,3,6,8-$Re_2Cl_4(PMe_2Ph)_4][ReO_4] \cdot CH_2Cl_2$[12] appeared on the walls of the tube. This complex is an exact analogue of the corresponding trimethylphosphine species[13] produced by air oxidation of $Re_2Cl_4(PMe_3)_4$. The first observation of the formation of the perrhenate anion upon exposure of a benzene solution of a $Re_2Cl_4(PR_3)_4$ compound to air was reported by Walton,[14] for the PEt_3 compound.

By analogy with the corresponding trimethylphosphine complex, **1a** exhibits very accessible redox chemistry ($E_{1/2}$(red) = −0.40, $E_{1/2}$(ox) = +0.75 V) and can be used as a starting material for studying one-electron oxidation and reduction processes (Scheme 1).

As we demonstrated previously,[1] the synthesis of the unprecedented 1,2,7,8-$Re_2Cl_4(PMe_3)_4$ molecule was based on the one-electron reduction of the corresponding 1,2,7-complex followed by nonredox substitution of a chloride by PMe_3. The same synthetic route applied in this work and involving one-electron reduction of 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ (**1a**) by cobaltocene in dichloromethane solution followed by substitution of Cl^- for the dimethylphenylphosphine affords 1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$ (**2**).

It should be mentioned that the 1,3,6,8-isomer of $Re_2Cl_4(PMe_2Ph)_4$ can be isolated using a more standard procedure, viz., by prolonged reflux of an ethanol suspension containing $Re_2Cl_8^{2-}$ and PMe_2Ph, and its crystal structure was reported.[4]

The one-electron oxidation of **1a** by $NOBF_4$ has also been accomplished in the present study, yielding a Re_2^{6+} core complex, $Re_2Cl_6(PMe_2Ph)_2$ (**3**) (Scheme 1). The $Re_2Cl_6(PR_3)_2$ (PR_3 = monodentate phosphine) class of compounds is well-

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(11) Cotton, F. A.; Dikarev, E. V. *Inorg. Chem.* **1996**, *35*, 4738.

(12) Crystal data for [1,3,6,8-$Re_2Cl_4(PMe_2Ph)_4][ReO_4] \cdot CH_2Cl_2$: monoclinic, $P2_1/c$ (No. 14), $a = 10.510(2)$ Å, $b = 33.11(1)$ Å, $c = 13.665(2)$ Å, $\beta = 111.31(2)°$, $V = 4430(2)$ Å^3, $Z = 4$, $\rho_{calc} = 2.102$ g/cm^3, $T = 213$ K, full-matrix refinement on F^2 (Nonius FAST area detector, SHELXL-93), R_1(on F_o) = 0.0561, wR_2(on F_o^2) = 0.1262, GOF = 1.128 for 432 parameters and 43 restraints, 5718 unique data (4860 with $I > 2\sigma(I)$). Re−Re = 2.2256(9) Å. See Supporting Information for other structure details.

(13) Cotton, F. A.; Jennings, J. G.; Price, A. C.; Vidyasagar, K. *Inorg. Chem.* **1990**, *29*, 4138.

(14) Brant, P.; Salmon, D. J.; Walton, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 4424.

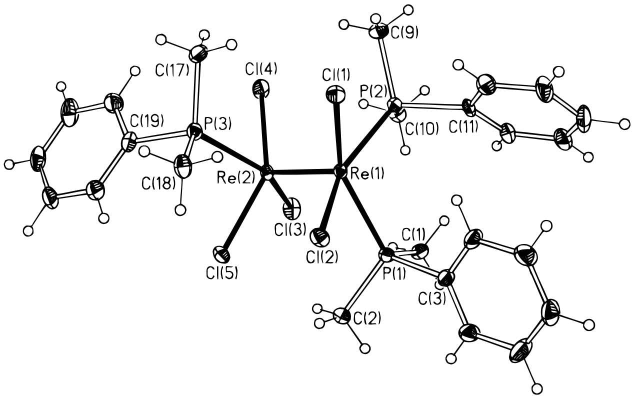

Figure 1. Perspective drawing of 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ (**1a**). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon atoms of the phenyl rings are not labeled for clarity. Hydrogen atoms are shown as spheres of arbitrary radius.

characterized, and direct preparative recipes have long been available.[15] $Re_2Cl_6(PMe_2Ph)_2$ has been obtained before by using methanol−HCl as the reaction medium, and its electrochemical behavior was investigated.[15] The formation of **3** was also observed in electrochemically oxidized solutions of $Re_2Cl_4(PMe_2Ph)_4$, through the reaction $[Re_2Cl_4(PMe_2Ph)_4]^{2+} + 2Cl^- \rightarrow Re_2Cl_6(PMe_2Ph)_2 + 2PMe_2Ph$.[4] The $Re_2Cl_6(PMe_2Ph)_2$ molecule, however, has not been defined structurally, so we attempted to obtain suitable crystals of **3** in order to complete the characterization of the whole series of dirhenium complexes containing dimethylphenylphosphine with Re−Re bond orders of 3, 3.5, and 4. The same route as the one we applied in the PMe_3 case,[1] namely, one-electron oxidation of **1a** in the presence of 1 equiv of $Bu^n{}_4NCl$, affords **3** in good yield. Physical and electrochemical properties of **3** correlate very well with those previously reported.

Description of Structures. 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ (1a) and 1,3,6-$Re_2Cl_5(PMe_2Ph)_3$ (1b). **1a** crystallizes in the triclinic space group $P\bar{1}$ with two noncentrosymmetric molecules per unit cell related by an inversion center. The molecule consists of two units, *cis*-$ReCl_2(PMe_2Ph)_2$ and $ReCl_3(PMe_2Ph)$, brought together by a Re−Re bond (Figure 1).The P−Re−P angle of 97.28(6)° (Table 2) is similar to the corresponding angle in the trimethylphosphine analogue (96.60(7)°).[10] Moreover, the averaged values of torsion angles Re−Re−P−C for **1a** (76.2, 48.7, 167.2°) are very close to those angles in 1,2,7-$Re_2Cl_5(PMe_3)_3$ (73.5, 54.6, 171.6°).[10] This demonstrates that dimethylphenylphosphine ligands are located in space in much the same way as those of trimethylphosphine, and there are no steric difficulties exceeding those in the case of PMe_3 when two PMe_2Ph groups are placed cis to each other on the rhenium atom.

An interesting feature of **1a** is that it exhibits an essentially staggered conformation with the torsion angles L−Re−Re−L being in the range 20.7−32.2° (Table 3), which is even larger than that for the PMe_3 analogue (11.0−20.0°).[10] Probably as a consequence of that, the Re−Re bond in **1a** (2.2313(4) Å) is the longest of all known Re_2^{5+} core monodentate ligated molecules having eclipsed conformations.

1,3,6-$Re_2Cl_5(PMe_2Ph)_3$ (**1b**) adopts the monoclinic group $P2_1/c$ with four molecules per unit cell. It is isostructural with the technetium analogue,[8] the only difference being that it shows no indication of the metal−metal unit disorder. The Re−Re bond in **1b**, 2.219(1) Å (Table 2), is typical for corresponding dirhenium molecules with a bond order of 3.5. In contrast to that of the 1,2,7-isomer (**1a**), the angle P−Re−P on the Re atom connected to two phosphines (Figure 2) is 153.5(1)°; i.e., dimethylphenylphosphine groups are trans to each other. Another difference is that molecule **1b**, like the molecules of all known 1,3,6-isomers, possesses an eclipsed conformation (Table 3). An explanation of this fact may be found by looking at the molecules of both isomers directly down the Re−Re axis (Figure 3). In molecule **1a**, the back portion, $ReCl_3P$ (Figure 3, left), has the possibility of counterclockwise rotation (as drawn) around the Re−Re bond to increase the angle P(2)−Re(1)−Re(2)−P(3) (115.5°) and to decrease the repulsion between the phosphine groups on P(2) and P(3). This gives a nearly staggered conformation to molecule **1a**. At the same time, the angle P(1)−Re(1)−Re(2)−P(3) still remains quite large (145.8°). The molecule 1,2,7-$Re_2Cl_5(PMe_3)_3$[10] has the same features but to a smaller extent (the corresponding angles are 103.1 and 159.1°), which is consistent with the smaller repulsive effect expected for the PMe_3 ligands. In the molecule of the 1,3,6-isomer (Figure 3, right), one can see that phosphine ligand P(3) is wedged between those of P(1) and P(2) (the angles P(1)−Re(1)−Re(2)−P(3) and P(2)−Re(1)−Re(2)−P(3) are 92.8 and 91.5°, respectively) and $ReCl_3P$ unit has no room for rotation on either side, thus locking the molecule into the eclipsed conformation.

Table 2. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ (**1a**) and 1,3,6-$Re_2Cl_5(PMe_2Ph)_3$ (**1b**)

	1a	**1b**
Re(1)−Re(2)	2.2313(4)	2.219(1)
Re(1)−P(1)	2.410(2)	2.431(4)
Re(1)−P(2)	2.402(2)	2.450(4)
Re(1)−Cl(1)	2.391(2)	2.344(4)
Re(1)−Cl(2)	2.371(2)	2.348(4)
Re(2)−P(3)	2.458(2)	2.437(4)
Re(2)−Cl(3)	2.361(2)	2.341(4)
Re(2)−Cl(4)	2.345(2)	2.335(4)
Re(2)−Cl(5)	2.297(2)	2.350(4)
P(1)−Re(1)−P(2)	97.28(6)	153.5(1)
P(1)−Re(1)−Cl(1)	146.89(5)	87.4(1)
P(1)−Re(1)−Cl(2)	80.19(6)	85.4(1)
P(2)−Re(1)−Cl(1)	85.72(6)	87.2(1)
P(2)−Re(1)−Cl(2)	155.17(5)	84.2(1)
Cl(1)−Re(1)−Cl(2)	83.54(6)	144.6(1)
Re(2)−Re(1)−P(1)	99.05(4)	102.7(1)
Re(2)−Re(1)−P(2)	97.58(4)	103.38(9)
Re(2)−Re(1)−Cl(1)	113.28(4)	111.2(1)
Re(2)−Re(1)−Cl(2)	107.23(4)	104.2(1)
P(3)−Re(2)−Cl(3)	151.88(5)	84.3(1)
P(3)−Re(2)−Cl(4)	84.83(6)	84.0(1)
P(3)−Re(2)−Cl(5)	82.56(6)	152.4(1)
Cl(3)−Re(2)−Cl(4)	87.38(6)	142.8(1)
Cl(3)−Re(2)−Cl(5)	88.71(6)	87.4(1)
Cl(4)−Re(2)−Cl(5)	145.21(5)	87.0(1)
Re(1)−Re(2)−P(3)	97.14(4)	102.82(9)
Re(1)−Re(2)−Cl(3)	110.91(4)	108.70(9)
Re(1)−Re(2)−Cl(4)	109.89(4)	108.25(9)
Re(1)−Re(2)−Cl(5)	103.78(4)	104.7(1)
P(1)−Re(1)−Re(2)−Cl(3)	32.15(6)	4.5(1)
P(2)−Re(1)−Re(2)−Cl(4)	28.44(6)	−3.7(1)
Cl(1)−Re(1)−Re(2)−P(3)	26.92(5)	0.6(1)
Cl(2)−Re(1)−Re(2)−Cl(5)	20.67(6)	0.7(2)

1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$ (2). This compound crystallizes in the triclinic space group $P\bar{1}$ with two crystallographically independent molecules possessing inversion centers at the midpoint of each Re−Re vector. A perspective view of one of the molecules is shown in Figure 4, and selected bond distances and angles are presented in Table 4. The average rhenium−rhenium distance in **2** is 2.260(1) Å, which is somewhat greater

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(15) Dunbar, K. R.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 5.

Table 3. Torsion Angles (deg) for $Re_2Cl_5P_3$ Core Molecules

	P(1)−Re−Re−Cl(3)[a]	P(2)−Re−Re−Cl(4)	Cl(1)−Re−Re−P(3)	Cl(2)−Re−Re−Cl(5)	ref
1,2,7-$Re_2Cl_5(PMe_2Ph)_3$	32.2	28.4	26.9	20.7	this work
1,2,7-$Re_2Cl_5(PMe_3)_3$	20.0	16.6	16.4	11.0	10
1,3,6-$Re_2Cl_5(PMe_2Ph)_3$	4.5	−3.7	0.6	0.7	this work
1,3,6-$Re_2Cl_5(PMe_3)_3$	5.8	−3.9	1.0	1.0	10
1,3,6-$Re_2Cl_5(PEt_3)_3$[b]	9.6	0.8	2.9	2.8	10
1,3,6-$Tc_2Cl_5(PMe_2Ph)_3$	5.8	−5.1	0.7	0.5	8
1,3,6-$W_2Cl_5(PMe_3)_3$	9.5	−7.8	−0.1	0.5	16

[a] Numbering of P and Cl atoms corresponds to Figure 3. [b] Disordered structure.

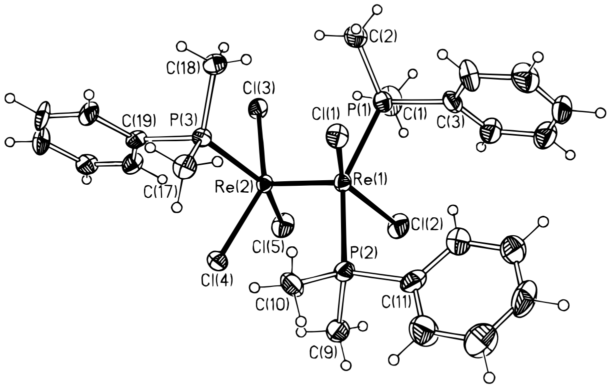

Figure 2. Perspective drawing of 1,3,6-$Re_2Cl_5(PMe_2Ph)_3$ (**1b**). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon atoms of the phenyl rings are not labeled for clarity. Hydrogen atoms are shown as spheres of arbitrary radius.

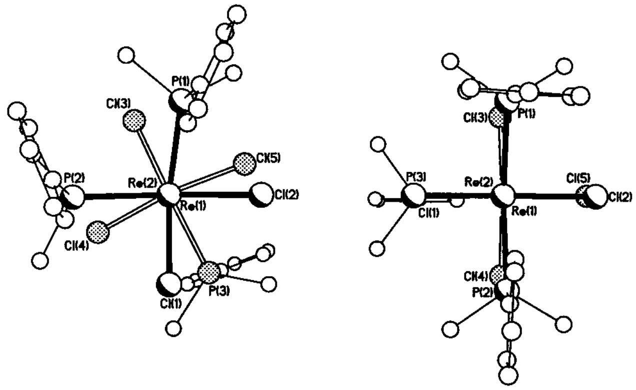

Figure 3. Views of the central part of molecules **1a** (left) and **1b** (right) directly down Re−Re axis. Atoms are represented as spheres of arbitrary radii. Only rhenium and its neighboring atoms are labeled for clarity. For the torsion angles, see Table 3.

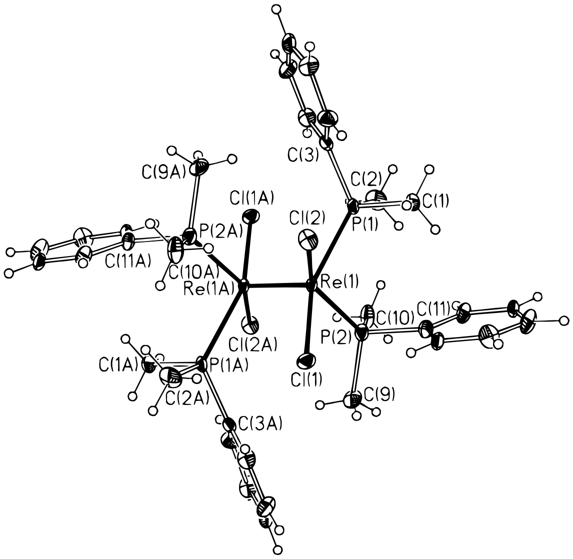

Figure 4. Perspective drawing of 1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$ (**2**). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon atoms of the phenyl rings are not labeled for clarity. Hydrogen atoms are shown as spheres of arbitrary radius.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Two Crystallographically Independent Molecules in the Crystal Structure of 1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$ (**2**)

Re(1)−Re(1A)	2.261(1)	Re(2)−Re(2A)	2.258(1)
Re(1)−P(1)	2.429(3)	Re(2)−P(3)	2.436(3)
Re(1)−P(2)	2.376(3)	Re(2)−P(4)	2.384(3)
Re(1)−Cl(1)	2.391(3)	Re(2)−Cl(3)	2.405(3)
Re(1)−Cl(2)	2.426(3)	Re(2)−Cl(4)	2.420(3)
P(1)−Re(1)−P(2)	93.1(1)	P(3)−Re(2)−P(4)	94.1(1)
P(1)−Re(1)−Cl(1)	149.2(1)	P(3)−Re(2)−Cl(3)	149.4(1)
P(1)−Re(1)−Cl(2)	80.7(1)	P(3)−Re(2)−Cl(4)	81.1(1)
P(2)−Re(1)−Cl(1)	87.7(1)	P(4)−Re(2)−Cl(3)	86.0(1)
P(2)−Re(1)−Cl(2)	144.6(1)	P(4)−Re(2)−Cl(4)	143.1(1)
Cl(1)−Re(1)−Cl(2)	81.0(1)	Cl(3)−Re(2)−Cl(4)	80.7(1)
Re(1A)−Re(1)−P(1)	103.96(9)	Re(2A)−Re(2)−P(3)	103.30(9)
Re(1A)−Re(1)−P(2)	96.02(9)	Re(2A)−Re(2)−P(4)	98.03(9)
Re(1A)−Re(1)−Cl(1)	106.62(9)	Re(2A)−Re(2)−Cl(3)	106.99(9)
Re(1A)−Re(1)−Cl(2)	119.33(9)	Re(2A)−Re(2)−Cl(4)	118.75(9)

than that in the 1,3,6,8-isomer of the same compound (2.241(1) Å).[4] The structure of **2** consists of two *cis*-$ReCl_2(PMe_2Ph)_2$ fragments that are rotated 180° with respect to each other, with the average P−Re−P angle being 93.6(1)°. This angle is smaller than the corresponding angle in parent molecule **1a** (97.3°) but exactly the same as that in 1,2,7,8-$Re_2Cl_4(PMe_3)_4$.[1] Thus, complex **2** is found to be the second example of a new 1,2,7,8-class of geometrical isomers of the $Re_2Cl_4(PR_3)_4$ stoichiometry, in which phosphine ligands coordinated to the same rhenium atom are cis to each other.

In the structure of **2**, both $Re_2Cl_4(PMe_2Ph)_4$ molecules are centrosymmetric and eclipsed (the torsion angles P−Re−Re−Cl range from 1.8 to 4.4°). This supports our model for the analogous trimethylphosphine molecule also being eclipsed.[1] In the PMe_3 case, there were some complications due to disorder, but in this case there are none.

The main difference in ligand arrangement between the two isomers of $Re_2Cl_4(PMe_2Ph)_4$ is that in 1,3,6,8 all Re−P and Re−Cl bonds are trans respectively to Re−P and Re−Cl bonds, whereas in 1,2,7,8 they are trans respectively to the Re−Cl and Re−P bonds at each end of the molecule. By comparing the Re−P and Re−Cl bond distances in these isomers, one can see clearly the existence of a strong trans influence, just as we mentioned before for the trimethylphosphine analogue.[1] Data concerning the trans influence on metal−ligand bond lengths for all known pairs of isomers having a $Re_2Cl_4P_4$ core are shown in Table 5.

Another interesting structural feature of complex **2** is that not all the phenyl rings of the phosphine ligands are directed parallel with the Re−Re vector. The orientation of the substituents on the phosphine ligands can be characterized by

Table 5. Trans-Effect in $Re_2Cl_4P_4$ Core Compounds (Bond Lengths in Å)

complex	Re−Re	$Re-P_{av}$	$Re-Cl_{av}$	Δ_{Re-L}[e]	ref
1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$[a]	2.261(1)	2.403(3)	2.409(3)	−0.006	this work
	2.258(1)	2.410(3)	2.413(3)	−0.003	
1,3,6,8-$Re_2Cl_4(PMe_2Ph)_4$	2.241(1)	2.418(1)	2.387(1)	+0.031	4
1,2,7,8-$Re_2Cl_4(PMe_3)_4$	2.2414(8)	2.373(7)	2.410(8)	−0.037	1
1,3,6,8-$Re_2Cl_4(PMe_3)_4$	2.247(1)	2.417(2)	2.380(2)	+0.037	13
α-$Re_2Cl_4(dppee)_2$[a−c]	2.250(1)	2.359(2)	2.394(2)	−0.035	17
	2.265(1)	2.363(2)	2.401(2)	−0.038	
β-$Re_2Cl_4(dppee)_2$[d]	2.242(3)	2.420(9)	2.365(8)	+0.055	17

[a] Two crystallographically independent molecules. [b] dppee = *cis*-$Ph_2PCH{=}CHPPh_2$. [c] 1,2,7,8-Isomer. [d] 1,3,6,8-Isomer. [e] $\Delta_{Re-L} = d_{Re-P} - d_{Re-Cl}$.

the torsion angles Re−Re−P−C. In the 1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$ molecule, only two phosphine phenyl rings are oriented parallel to the Re−Re bond with ∠Re−Re−P−C_{Ph} being 168.1(4)° (averaged for two molecules), while the other two rings are projected "perpendicular" to the same metal−metal axis with the corresponding torsion angle being 67.2(5)°. The latter orientation is seen here for the first time in any isomer in the whole $M_2X_{8-n}(PMe_2Ph)_n$ ($n = 2, 3, 4$) class of compounds; in all other cases only the "parallel" orientation was observed (Table 6). Recently,[18] the supposition was made that dimethylphenylphosphine complexes with more than one orientation of the dimetal unit could possess different conformational isomers in the crystal structure, because phenyl groups that lie parallel in the primary orientation must be directed perpendicular in the minor orientation. However, there is no evidence of conformational isomerism for disordered dinuclear molecules in the literature to date. It may be more reasonable to suggest that, because the minor orientations have very low populations, one simply cannot see the carbon atoms for these secondary molecules: 2% in 1,3,6,8-$Re_2Cl_4(PMe_2Ph)_4$,[4] 5.7% in 1,3,6,8-$Tc_2Cl_4(PMe_2Ph)_4$,[18] and 1.81/1.46% in 1,3,6-$Tc_2Cl_5(PMe_2Ph)_3$.[8]

Orientation of half of the phenyl rings in complex **2** perpendicular to the Re−Re vector does not arise solely from a cis-arrangement of two phosphine ligands on a rhenium atom, since such an arrangement is not observed in the *cis*-$ReCl_2(PMe_2Ph)_2$ part of 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ (**1a**). More likely, this is an effect of packing forces: the molecular volume for the 1,2,7,8-isomer is about 26 Å^3 smaller than that for the 1,3,6,8-isomer.

1,7-$Re_2Cl_6(PMe_2Ph)_2$ (3). Crystals of **3** adopt the triclinic $P\bar{1}$ space group. Each of the two crystallographically independent molecules resides on an inversion center to give an eclipsed geometry with C_{2h} symmetry (the torsion angles L−Re−Re−L are between 0.4 and 6.5°). The arrangement of PMe_2Ph ligands (Figure 5) and most of the distances and angles in both molecules of **3** are in good agreement with those in the other known 1,7-$Re_2Cl_6(PR_3)_2$ structures.[2]

The Re−Re distances (2.215(1) and 2.212(1) Å for the two molecules) are consistent with the presence of a quadruple bond. Unlike the case of the trimethylphosphine analogue, no disorder of the dimetal unit was found in the crystal structure of **3**. In our previous work,[1] we discussed some discrepancies in metal to ligand distances between ordered and disordered structures for the mixed chloride/phosphine complexes of the dirhenium core. As in nondisordered structures of $Re_2Cl_6(PEt_3)_2$[20] and $Re_2Cl_6(PMePh_2)_2$,[21] the Re−Cl distances in the molecule of **3** (Table 7) show an unambiguous trans influence due to the PMe_2Ph ligands. The Re−Cl bonds trans to the Re−P bonds are about 0.04 Å longer than those that are cis. Also, the Re−Re−Cl_{transP} angles are about 12° larger than the Re−Re−Cl_{cisP} angles. The sweeping back of the Cl atom trans to the phosphorus has been attributed to the steric interaction between this chlorine atom and the phosphine group attached to the opposite rhenium atom.[21]

In conclusion, let us look at the trend in metal−metal distances for the title dirhenium complexes. As we mentioned before, prior to this work, the series of $[1,3,6,8\text{-}Re_2Cl_4(PMe_2Ph)_4]^{n+}$ ($n = 0, 1, 2$) molecules have been structurally characterized. It was found that for this dinuclear system having the same ligand environment with Re−Re bond orders in the range 3.0−4.0 the Re−Re distances do not respond in a direct way to δ bond order increases. On going from Re_2^{4+} to Re_2^{5+} (Table 8), there is a contraction of 0.023 Å, while in going from Re_2^{5+} to Re_2^{6+}, there is no statistically significant change (0.003 Å). That observation was attributed to the competition between the formal bond order change and the charge effect, which work in opposite directions. We see the same picture when we look at the series of dimethylphenylphosphine complexes 1,3,6,8-$Re_2Cl_4(PMe_2Ph)_4$, 1,3,6-$Re_2Cl_5(PMe_2Ph)_3$, and 1,7-$Re_2Cl_6(PMe_2Ph)_2$ (Table 8). However, the structures of **2**, **1a**, and **3** display statistically significant changes in the Re−Re bond lengths (0.029 and 0.017 Å). The same trend was observed for the series of trimethylphosphine analogues (Table 8). These results show that the effect of bond order changes can be slightly dominant over an effect of charge increase, depending on the molecular stereochemistry.

Spectroscopic Data. The ^{31}P NMR spectra of complexes **2** and **3** in CD_2Cl_2 exhibit singlet signals at δ −20.67 and 0.47 ppm, respectively. These results are in accord with expectation for these symmetric structures in which all phosphines are chemically equivalent. Both **2** and **3** are stable in solution, their spectra not changing with time. The present results correspond very well with resonances reported[1] for PMe_3 analogues: 1,2,7,8-$Re_2Cl_4(PMe_3)_4$ (δ −20.46 ppm) and 1,7-$Re_2Cl_6(PMe_3)_2$ (δ 3.05 ppm).[1]

The X-band ESR spectra of dichloromethane glasses of **1a** and **1b** confirm the paramagnetism of these complexes. These spectra are very similar, centered at about 2750 G, giving a *g* value of about 2.45. As in the case of the PMe_3 analogues, a complex pattern is observed showing a considerable amount of hyperfine coupling to the two rhenium isotopes (^{185}Re and ^{187}Re, each with $I = {}^5/_2$) and phosphorus ($I = {}^1/_2$) nuclei. A series of broad bands, consisting of parallel and perpendicular orientation lines, extends from 1500 to 4500 G. The values of $g_\perp$ and $g_\parallel$ cannot be determined because of the complexity of the spectral patterns.[22]

The mass spectral data for all reported complexes show that rupture of the metal−metal bond is a major fragmentation process for these molecules under the experimental conditions.

Electrochemistry. It is known that the mixed halide/phosphine complexes of Re_2^{n+} ($n = 6, 5, 4$) exhibit the most

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(16) Cotton, F. A.; Dikarev, E. V. *Inorg. Chem.* **1995**, *34*, 3809.
(17) Bakir, M.; Cotton, F. A.; Falvello, L. R.; Vidyasagar, K.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2460.
(18) Burns, C. J.; Burrell, A. K.; Cotton, F. A.; Haefner, S. C.; Sattelberger, A. P. *Inorg. Chem.* **1994**, *33*, 2257.
(19) Cotton, F. A.; Daniels, L. M.; Powell, G. L.; Kahaian, A. J.; Smith, T. J.; Vogel, E. F. *Inorg. Chim. Acta* **1988**, *144*, 109.
(20) Bennett, M. J.; Cotton, F. A.; Foxman, B. M.; Stokely, P. F. *J. Am. Chem. Soc.* **1967**, *89*, 2759.
(21) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chim. Acta* **1988**, *144*, 17.
(22) Cotton, F. A.; Pedersen, E. *J. Am. Chem. Soc.* **1975**, *97*, 303.
(23) Root, D. R.; Blevins, C. H.; Lichtenberger, D. L.; Sattelberger, A. P.; Walton, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 953.

Table 6. Averaged Torsion Angles Re−Re−P−C (deg) for $M_2Cl_{8-x}(PMe_2Ph)_x$ (M = Re, Tc, Mo; x = 2, 3, 4) Molecules

	Re−Re−P−C_{Ph}	Re−Re−P−C_{Me}	Re−Re−P−C_{Me}	ref
1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$	67.2	−177.7	−64.8	this work
	168.1	−78.6	50.1	
1,2,7-$Re_2Cl_5(PMe_2Ph)_3$	167.2	−76.2	48.7	this work
1,7-$Re_2Cl_6(PMe_2Ph)_2$	178.4	−65.3	61.9	this work
1,3,6-$Re_2Cl_5(PMe_2Ph)_3$	176.8	−65.5	60.6	this work
1,3,6,8-$Re_2Cl_4(PMe_2Ph)_4$	174.7	−69.8	59.5	4
[1,3,6,8-$Re_2Cl_4(PMe_2Ph)_4]^+$	176.8	−67.3	59.9	4
[1,3,6,8-$Re_2Cl_4(PMe_2Ph)_4]^{2+}$	175.3	−68.2	58.5	4
1,3,6,8-$Tc_2Cl_4(PMe_2Ph)_4$	174.6	−69.0	58.5	18
1,3,6-$Tc_2Cl_5(PMe_2Ph)_3$	176.9	−66.5	60.0	8
1,3,6,8-$Mo_2Cl_4(PMe_2Ph)_4$	174.8	−68.6	58.6	19

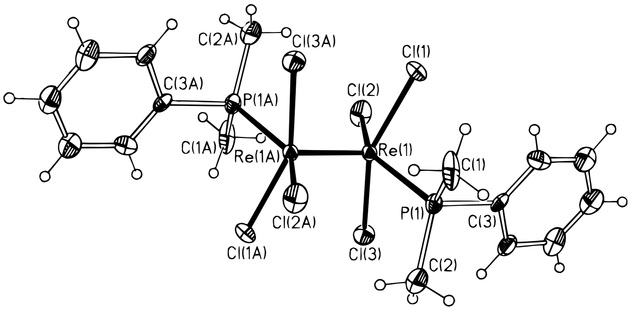

Figure 5. Perspective drawing of 1,7-$Re_2Cl_6(PMe_2Ph)_2$ (**3**). Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon atoms of the phenyl rings are not labeled for clarity. Hydrogen atoms are shown as spheres of arbitrary radius.

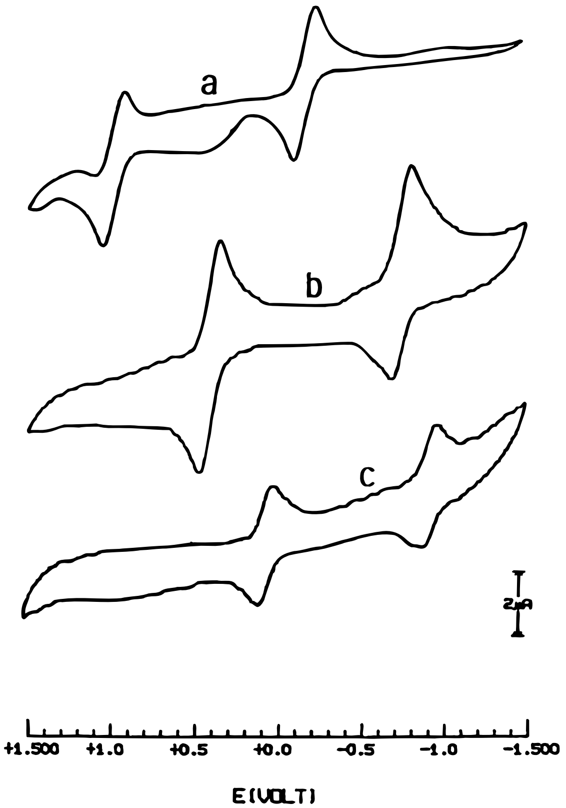

Figure 6. Cyclic voltammograms of (a) 1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$ (**2**), (b) 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ (**1a**), and (c) 1,7-$Re_2Cl_6(PMe_2Ph)_2$ (**3**) in dichloromethane solutions (0.1 M TBAH) at room temperature. For the values of half-wave potentials, see Table 9.

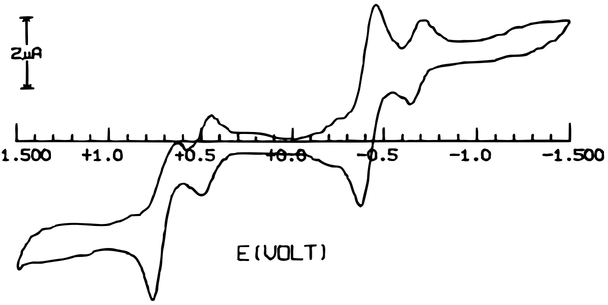

Figure 7. Cyclic voltammogram of the mixture of 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ (**1a**) and 1,3,6-$Re_2Cl_5(PMe_2Ph)_3$ (**1b**) in dichloromethane solution (0.1 M TBAH) at room temperature. For the values of half-wave potentials, see Table 9.

Table 7. Selected Bond Distances (Å) and Angles (deg) for Two Crystallographically Independent Molecules in the Crystal Structure of 1,7-$Re_2Cl_6(PMe_2Ph)_2$ (**3**)

Re(1)−Re(1A)	2.215(1)	Re(2)−Re(2A)	2.212(1)
Re(1)−P(1)	2.440(4)	Re(2)−P(2)	2.445(5)
Re(1)−Cl(1)	2.306(5)	Re(2)−Cl(4)	2.320(6)
Re(1)−Cl(2)	2.350(5)	Re(2)−Cl(5)	2.349(5)
Re(1)−Cl(3)	2.304(5)	Re(2)−Cl(6)	2.298(5)
P(1)−Re(1)−Cl(1)	85.2(2)	P(2)−Re(2)−Cl(4)	84.9(2)
P(1)−Re(1)−Cl(2)	146.0(2)	P(2)−Re(2)−Cl(5)	146.5(2)
P(1)−Re(1)−Cl(3)	84.7(2)	P(2)−Re(2)−Cl(6)	85.1(2)
Cl(1)−Re(1)−Cl(2)	87.9(2)	Cl(4)−Re(2)−Cl(5)	87.9(2)
Cl(1)−Re(1)−Cl(3)	153.3(2)	Cl(4)−Re(2)−Cl(6)	153.4(2)
Cl(2)−Re(1)−Cl(3)	86.8(2)	Cl(5)−Re(2)−Cl(6)	87.0(2)
Re(1A)−Re(1)−P(1)	98.9(1)	Re(2A)−Re(2)−P(2)	98.6(1)
Re(1A)−Re(1)−Cl(1)	103.4(1)	Re(2A)−Re(2)−Cl(4)	102.8(1)
Re(1A)−Re(1)−Cl(2)	115.2(1)	Re(2A)−Re(2)−Cl(5)	115.0(1)
Re(1A)−Re(1)−Cl(3)	102.5(1)	Re(2A)−Re(2)−Cl(6)	103.0(1)

extensive and best defined redox chemistry of any class of multiply bonded dimetal species.[2] Since the cis geometry was unknown for the dirhenium complexes containing monodentate phosphines prior to our work, one of our interests was to obtain electrochemical characteristics for the 1,2,7- and 1,2,7,8-isomers and to compare these with respective data for 1,3,6- and 1,3,6,8-compounds (Table 9). The experimental CV traces for the title complexes are shown in Figures 6 and 7.

The paramagnetic 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ (**1a**) exhibits electrochemistry which is consistent with the presence of the Re_2^{5+} core. The cyclic voltammogram of **1a** reveals two reversible one-electron redox processes, thus confirming that conversions of both types ($Re_2^{5+} \rightarrow Re_2^{4+}$ and $Re_2^{5+} \rightarrow Re_2^{6+}$) are equally accessible with one-electron reduction at $E_{1/2} = -0.40$ V and one-electron oxidation at $E_{1/2} = +0.75$ V. Both redox reactions have been accomplished chemically in the present study, resulting in **2** and **3**, respectively. The reversibility of the redox couples suggests that subsequent addition or removal of a δ^* electron from the Re_2^{5+} core of **1a** does not induce any major structural change.

The CV characterization for 1,3,6-$Re_2Cl_5(PMe_2Ph)_3$ (**1b)** was done before[4] through the reaction [1,3,6,8-$Re_2Cl_4(PMe_2Ph)_4]^+$ + $Cl^- \rightarrow$ 1,3,6-$Re_2Cl_5(PMe_2Ph)_3$ + PMe_2Ph carried out in the electrochemical cell. We obtained this complex as a mixture with 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ and performed electrochemical

Table 8. Change of the Re−Re Bond Lengths (Å) for the Series of Re_2^{n+} (n = 4, 5, 6) Complexes

Re_2^{4+}	1,3,6,8-$Re_2Cl_4(PMe_2Ph)_4$		1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$	1,2,7,8-$Re_2Cl_4(PMe_3)_4$
	2.241(1)		**2.260(1)**[a]	**2.2414(8)**
	0.023	0.022	0.029	0.015
Re_2^{5+}	[1,3,6,8-$Re_2Cl_4(PMe_2Ph)_4]^+$	1,3,6-$Re_2Cl_5(PMe_2Ph)_3$	1,2,7-$Re_2Cl_5(PMe_2Ph)_3$	1,2,7-$Re_2Cl_5(PMe_3)_3$
	2.218(1)	**2.219(1)**	**2.2313(4)**	**2.226(1)**
	0.003	0.005	0.017	0.018
Re_2^{6+}	[1,3,6,8-$Re_2Cl_4(PMe_2Ph)_4]^{2+}$	1,7-$Re_2Cl_6(PMe_2Ph)_2$		1,7-$Re_2Cl_6(PMe_3)_2$
	2.215(2)	**2.214(1)**[a]		**2.208(1)**

[a] Averaged for two crystallographically independent molecules.

Table 9. Electrochemical Data for $Re_2Cl_5(PR_3)_3$ and $Re_2Cl_4(PR_3)_4$ Isomers (R_3 = Me_3, Me_2Ph)

$Re_2Cl_5(PR_3)_3$	$E_{1/2}$(red)	$E_{1/2}$(ox)	ref
1,2,7-$Re_2Cl_5(PMe_2Ph)_3$[a]	−0.40	+0.75	this work
1,3,6-$Re_2Cl_5(PMe_2Ph)_3$[a]	−0.67	+0.48	this work
1,2,7-$Re_2Cl_5(PMe_3)_3$[a]	−0.48	+0.68	10
1,3,6-$Re_2Cl_5(PMe_3)_3$[a]	−0.75	+0.46	10

$Re_2Cl_4(PR_3)_4$	$E_{1/2}$(ox)(1)	$E_{1/2}$(ox)(2)	ref
1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$[a]	−0.17	+0.98	this work
1,3,6,8-$Re_2Cl_4(PMe_2Ph)_4$[b]	−0.30	+0.83	14
1,2,7,8-$Re_2Cl_4(PMe_3)_4$[a]	−0.16	+1.12	1
1,3,6,8-$Re_2Cl_4(PMe_3)_4$[c]	−0.23	+0.96	23

[a] Volts vs Ag/AgCl in CH_2Cl_2−0.1 M TBAH at room temperature. [b] Volts vs SSCE in CH_2Cl_2−0.2 M TBAH at room temperature. [c] Volts vs Ag/AgCl in CH_2Cl_2−0.2 M TBAH at room temperature.

measurements (Figure 7) under the same conditions for both isomers (V vs Ag/AgCl in CH_2Cl_2−0.1 M TBAH at room temperature). Again, there is a strong negative shift (~0.27 V) for both $E_{1/2}$(ox) and $E_{1/2}$(red) potentials for the complex with a trans-arrangement of the phosphine ligands. This difference in $E_{1/2}$ potentials agrees well with the corresponding values for another pair of 1,2,7-/1,3,6-isomers of PMe_3 analogues (Table 9). Figure 7 also illustrates that isomers **1a** and **1b** can be recognized by CV when present together in the solution as was previously shown for the 1,2,7-/1,3,6-$Re_2Cl_5(PMe_3)_3$ couple.[11] Thus, voltammetric measurements can serve as a tool for investigation of the possible isomerization processes in this case.

The diamagnetic 1,2,7,8-$Re_2Cl_4(PMe_2Ph)_4$ (**2**) complex with an Re_2^{4+} core exhibits, as expected, two one-electron oxidations with half-wave potentials of −0.17 and +0.98 V vs Ag/AgCl. Comparison of these data with the corresponding characteristics of 1,2,7,8-$Re_2Cl_4(PMe_3)_4$ ($E_{1/2}$(ox)(1) = −0.16 V and $E_{1/2}$(ox)(2) = +1.12 V) shows very close similarity in electrochemical behavior for the two compounds.

Corresponding values reported for 1,3,6,8-$Re_2Cl_4(PMe_2Ph)_4$[14] at $E_{1/2}$(ox)(1) = −0.30 and $E_{1/2}$(ox)(2) = +0.83 V clearly indicate the same trend noted for cis,trans pairs of dirhenium complexes; that is, the $E_{1/2}$ values become more positive for cis-isomers. Thus, electrochemistry provides additional confirmation of the identity and stability of cis,trans pairs of isomers in both 1,2,7/1,3,6 and 1,2,7,8/1,3,6,8 cases.

The diamagnetic complex 1,7-$Re_2Cl_6(PMe_2Ph)_2$ (**3**) possesses an accessible first reduction at +0.06 V, which reversibly yields the monoanion $[Re_2Cl_6(PMe_2Ph)_2]^-$, as monitored by CV. This value falls within the range +0.06 to −0.37 V reported [2] for the $Re_2Cl_6(PR_3)_2$ class.

Complex **3** also exhibits a second reduction at a quite negative potential, with $E_{1/2}$(red)(2) = −0.93 V. This process is associated with the reduction of $[Re_2Cl_6(PMe_2Ph)_2]^-$ to the corresponding unstable dianion. Reported values[2] for the second reduction range from −0.85 to −0.99 V for this type of dirhenium structure. This process is reversible for the complex containing PMe_2Ph, as demonstrated by CV.

Concluding Remarks

We have now found that two dimethylphenylphosphine molecules can be coordinated in a cis mode at a rhenium center, in the same manner as PMe_3, affording novel 1,2,7-$Re_2Cl_5(PR_3)_3$ and 1,2,7,8-$Re_2Cl_4(PR_3)_4$ stereochemical types. Steric and electronic properties of phosphines are both crucial to stabilize the cis-geometrical structures, but the role of solvent is also very important. The solubilities of the starting material, intermediates, and products are apparently critical for the chemical and stereochemical control of the reaction route. In all three solvents explored in the present work (benzene, alcohol, and acetonitrile), the reduction to Re^{II}−Re^{III} compounds occurs at room temperature, but reaction times and products are different.

Reaction in benzene is a heterogeneous process, both starting material and products being insoluble in this medium, and 3−4 days are required to complete the formation of 1,2,7-$Re_2Cl_5(PMe_2Ph)_3$ (**1a**). However, even over such a prolonged time, we have not seen any indication of the dimethylphenylphosphine analogue of $Re_2Cl_6(PMe_3)_4$. The most likely explanation of this fact can be based on the different solubilities in C_6H_6 of the PMe_3 and PMe_2Ph products of the stoichiometry $Re_2Cl_6(PR_3)_4$. The latter might be an intermediate step on the way to **1a**, but because of its good solubility in benzene, it readily converts to the insoluble Re_2^{5+} product.

Reaction in alcohol is also heterogeneous, but in this case, the products are completely soluble. The transformation of

$Re_2Cl_8^{2-}$ proceeds much faster than it does in benzene, with the 1,2,7-isomer as the only product. The analogous reaction with PMe_3 is known to be similar.

The most interesting result was obtained in a homogeneous process using acetonitrile as the solvent. The reaction takes place immediately, and the product is a mixture of the 1,2,7- (**1a**) and 1,3,6-isomers (**1b**) of $Re_2Cl_5(PMe_2Ph)_3$. One possible explanation can involve the partial isomerization of the 1,2,7- to the 1,3,6-complex in the presence of free phosphine, since we have not observed isomerization in a neat acetonitrile solution of **1a**. On the other hand, there might be two parallel processes in this homogeneous system: one similar to those found in other solvents, leading to the 1,2,7-isomer, and another one giving the 1,3,6-species directly.

The mechanisms of all these reactions are not yet well understood. The interactions of $Re_2Cl_8^{2-}$ with phosphines, which include substitution, reduction, and isomerization stages, seem very promising model processes to examine. The study of the influence of solvent on the reaction pathway with different phosphines is to be continued.

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Supporting Information Available: Crystal structure drawings (9 pages). Five X-ray crystallographic files, in CIF format, are available on the Internet only. Ordering and access information is given on any current masthead page.

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