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Mixed Chloride/Phosphine Complexes of the Dirhenium Core. 6. Rare or Unprecedented Isomers of $[Re_2Cl_6(PR_3)_2]$ Stoichiometry

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Several new paramagnetic dirhenium(II,III) anions of the formula $[Re_2Cl_6P_2]^-$ (P_2 = $(PPr^n{}_3)_2$ (**1**), $(PEt_2Ph)_2$ (**2**), dppp (**3**)) have been isolated in the form of their tetrabutylammonium salts as the kinetic products in reactions of $[Re_2Cl_8]^{2-}$ with an appropriate phosphine ligand. All three complexes have been characterized in solution by cyclic voltammetry, ESR, and mass spectroscopy. Three different isomeric forms of the $[Re_2Cl_6P_2]$ core have been recognized in the solid state by X-ray crystallography. The known 1,7-isomer (C_{2h}) with a centrosymmetric disposition of phosphine groups was found for $PPr^n{}_3$ (**1a**) and PEt_2Ph (**2**) ligands. The compound $[Bu^n{}_4N][Re_2Cl_6(PPr^n{}_3)_2]$ was also crystallized in the unprecedented form of a 1,6-isomer (C_2) (**1b**) which can be derived from **1a** by a 90° rotation of the ligands around the metal−metal bond. For the diphosphine, a C_s isomer of $[Re_2Cl_6(dppp)]^-$ (**3**) was discovered having the dppp ligand chelating on one rhenium atom. Crystallographic data are as follows: for **1a**, monoclinic space group $P2_1/n$ with $a = 12.758(1)$ Å, $b = 15.755(5)$ Å, $c = 24.160(3)$ Å, $\beta = 104.22(1)°$, and $Z = 4$; for **1b**, monoclinic space group $P2_1/c$ with $a = 16.3355(8)$ Å, $b = 12.656(1)$ Å, $c = 22.892(2)$ Å, $\beta = 94.735(6)°$, and $Z = 4$; for **2**, triclinic space group $P\bar{1}$ with $a = 11.868(1)$ Å, $b = 12.125(2)$ Å, $c = 15.375(3)$ Å, $\alpha = 88.01(1)°$, $\beta = 82.64(1)°$, $\gamma = 88.47(1)°$, and $Z = 2$; for **3**, triclinic space group $P\bar{1}$ with $a = 11.8986(4)$ Å, $b = 11.913(1)$ Å, $c = 18.383(2)$ Å, $\alpha = 102.23(2)°$, $\beta = 108.003(5)°$, $\gamma = 97.38(1)°$, and $Z = 2$.

Introduction

The first report of partial replacement of Cl^- ligands by phosphines in the $[Re_2Cl_8]^{2-}$ ion appeared in 1965.[1] Since then, of course, a very large number of such reactions have been reported and, for the most part, the products have been structurally defined by X-ray crystallography.[2] Beginning with the report[3] of the preparation of 1,3,6,8-$Re_2Cl_4(PEt_3)_4$ nine years later, the concept of reductive substitution came into the picture. In spite of the proliferation of compounds of the general type $[Re_2X_{8-n}(PR_3)_n]$ ($n = 1-4$), both neutral and ionic, the "rules of the game" so to speak, that is, how the substitution reactions occur, and how to control them so as to obtain a desired product, as well as an understanding of which of the many isomers that can be envisioned actually exist, remained poorly understood.

Several years ago, we began to take a systematic approach to elucidating the "rules of the game", and we present here our latest report,[4] wherein we deal with the simplest case (barring $[Re_2Cl_7PR_3]$, where only one isomer[5] can exist), namely, $[Re_2Cl_6(PR_3)_2]$. To summarize briefly the position to date for cases where $n = 2-4$, we note that the most often characterized species are the 1,3,6,8 isomers[3,4d,6] of the $Re_2X_4(PR_3)_4$ (**I**) molecules with a trans arrangement of phosphine ligands on each end of the molecule. The second isomer of that formula, namely, the 1,2,7,8 isomer, having PR_3 groups cis on each rhenium atom, was recently discovered by us[4a] and is now known for three different phosphines.[4a−c] Replacing one phosphine ligand by the halide in each of the isomers of **I** gives the isomeric compounds of composition $[Re_2X_5(PR_3)_3]$ (**II**), namely, 1,2,7 and 1,3,6, both of which are now well established.[4b,e,7] Finally, for the $[Re_2X_6(PR_3)_2]$ stoichiometry (**III**), the only form known so far corresponds to the centrosymmetric 1,7 arrangement.[4a,b,8] Neither the 1,2, 1,3, nor 1,6 isomers have yet been made.

Our previous experience with these compounds suggests that there are two structural restraints on possible isomers: (i) monodentate phosphines cannot be located facing each other across the metal−metal bond; (ii) the number of phosphine groups on each rhenium atom may not differ by more than 1.

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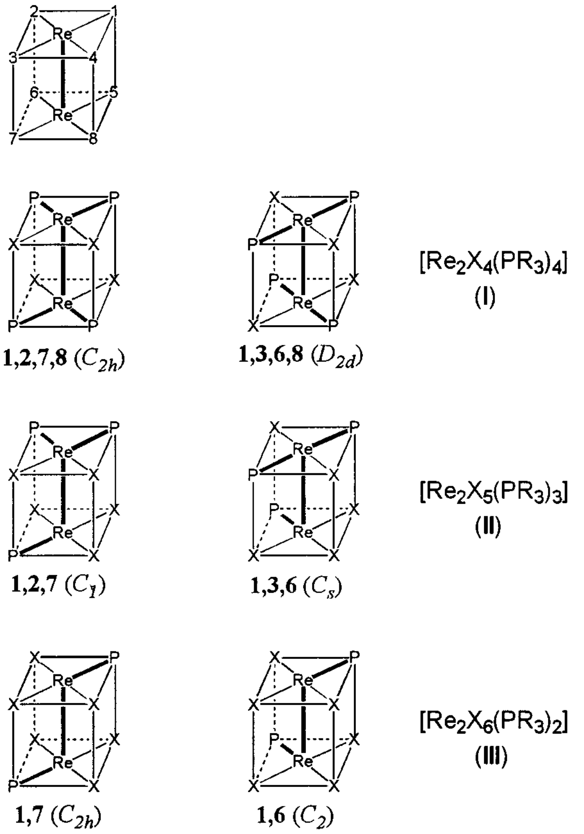
Chart 1



In view of these restraints, 1,2 or 1,3 isomers are improbable for the $[Re_2X_6(PR_3)_2]$ stoichiometry; the 1,6 isomer (Chart 1), also not yet seen, and not forbidden, also seems improbable. The only difference between the pair of isomers **III** as compared to those of types **I** and **II** is that either one can be obtained from the other merely by a 90° rotation around the metal−metal vector and no breaking of bonds is needed to accomplish isomerization. Since the rotational barrier will not exceed ca. 15 kcal mol^{-1}, it would seem impossible to observe the 1,6 isomer in solution, but its occurrence in the solid state is not necessarily precluded.

We have made numerous unrewarded attempts to isolate a 1,6 isomer for neutral quadruply bonded $Re_2Cl_6(PR_3)_2$ molecules. However, we have now managed to crystallize this isomer in its anionic form, $[Re_2Cl_6(PPr^n_3)_2]^-$ (**1b**), with a Re−Re bond order of 3.5. The previously known 1,7 isomer is represented here by the $[Re_2Cl_6(PR_3)_2]^-$ anions for $R_3 = Pr^n_3$ (**1a**) and Et_2Ph (**2**). As for the second of the structural constraints noted above, it has been overcome by the use of a bidentate phosphine and the anion $[Re_2Cl_6(\eta^2\text{-dppp})]^-$ (**3**) also described in this paper.

Experimental Section

General Procedures. All of the syntheses and purifications were carried out under an atmosphere of N_2 in standard Schlenkware. All solvents were freshly distilled under N_2 from suitable drying agents. Chemicals were purchased from the following commercial sources and used as received: PEt_2Ph, PPr^n_3, and 1,3-bis(diphenylphosphino)propane (dppp), Strem Chemicals; $[Bu^n_4N]_2[Re_2Cl_8]$, Aldrich, Inc.

Physical Measurements. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. A stream of nitrogen was bubbled through the solution during the measurements. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the Ag/AgCl electrode at room temperature. Under our experimental conditions, $E_{1/2} = +0.47$ V vs Ag/AgCl for the ferrocenium/ferrocene couple. Voltammetric experiments were 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. Elemental analyses were done by Canadian Microanalytical Services, Ltd. X-band ESR spectra of dichloromethane glasses were recorded at 100 K with a frequency of 9.4 GHz on a Bruker ESR 300 spectrometer. The negative FAB/DIP mass spectra were acquired using a VG Analytical 70S high-resolution, double-focusing, sectored (EB) mass spectrometer. Samples for analyses were prepared by mixing a solution of each compound in CH_2Cl_2 with an NBA matrix on the direct insertion probe tip.

Synthesis. $[Bu^n_4N][Re_2Cl_6(PPr^n_3)_2]$ (1). To a suspension containing $[Bu^n_4N]_2[Re_2Cl_8]$ (0.321 g, 0.28 mmol) in 15 mL of 1-propanol was added 1 mL of PPr^n_3. The mixture was stirred for 3 days at room temperature to give a green-brown solution. All volatile components were removed under reduced pressure to leave a brown-green residue, which was dried overnight in a vacuum and then extracted with 20 mL of hexanes. The extract was filtered, reduced in volume by half, and placed in the freezer at −20 °C to afford green crystals (total mass 0.211 g). They were recrystallized from diethyl ether to give three types of crystalline products: $[Bu^n_4N][Re_2Cl_6(PPr^n_3)_2]$ (**1**) in the form of visually distinguishable grass-green (**1a**) and pale-green (**1b**) needles and green plates of $Re_2Cl_5(PPr^n_3)_3$.[4e,9]

Anal. Calcd for $Re_2P_2NCl_6C_{34}H_{78}$: N, 1.22; C, 35.57; H, 6.85. Found: N, 1.25; C, 35.53; H, 6.97. For $[Re_2Cl_6(PPr^n_3)_2]^-$: −FAB/DIP (NBA/CH_2Cl_2; *m/z*) 904 ($[M]^-$), 869 ($[M-Cl]^-$), 836 ($[M-2Cl]^-$), 746 ($[M-PPr_3]^-$), 709 ($[M-PPr_3-Cl]^-$), 586 ($[M-2PPr_3]^-$), 549 ($[M-2PPr_3-Cl]^-$), 514 ($[M-2PPr_3-2Cl]^-$); ESR (CH_2Cl_2, 100 K) centered at 2691 G, $g = 2.50$; CV (CH_2Cl_2, 22 °C, V vs Ag/AgCl) $E_{1/2}(\text{ox}) = -0.12$.

$[Bu^n_4N][Re_2Cl_6(PEt_2Ph)_2]$ (2). Method 1. To a suspension containing $[Bu^n_4N]_2[Re_2Cl_8]$ (0.228 g, 0.2 mmol) in 15 mL of 1-propanol was added 1 mL of PEt_2Ph. The mixture was stirred at room temperature to give a green-brown solution in 2 h. All volatile components were removed under vacuum to leave an oily green-brown solid, which was washed with diethyl ether (15 mL) and toluene (10 mL) to leave a green crystalline solid. It was dried and dissolved in 10 mL of dichloromethane. The solution was then layered with 15 mL of hexanes to afford green crystals of **2** in a few hours. Yield: 0.192 g (83%).

Method 2. To a suspension containing $[Bu^n_4N]_2[Re_2Cl_8]$ (0.232 g, 0.2 mmol) in 15 mL of benzene was added 1 mL of PEt_2Ph. The mixture was stirred at room temperature for 7 days. All volatile components were then removed under reduced pressure to leave a green-brown residue. It was washed with hexanes (2 × 15 mL), dried, and dissolved in a mixture of 10 mL of toluene and 5 mL of dichloromethane. The resulting green solution was filtered and layered with 15 mL of hexanes. Green crystals of **2** came out in a few days at room temperature. Yield: 0.129 g (54%). Anal. Calcd for $Re_2P_2NCl_6C_{36}H_{66}$: N, 1.21; C, 37.28; H, 5.73. Found: N, 1.18; C, 37.40; H. 5.41. For $[Re_2Cl_6(PEt_2Ph)_2]^-$: −FAB/DIP for (NBA/CH_2Cl_2, *m/z*) 750 ($[M-PEt_2Ph]^-$), 586 ($[M-2PEt_2Ph]^-$), 551 ($[M-2PEt_2Ph-Cl]^-$); ESR (CH_2Cl_2, 100 K) centered at 2682 G, $g = 2.49$; CV (CH_2Cl_2, 22 °C, V vs Ag/AgCl) $E_{1/2}(\text{ox}) = 0.02$, $E_{p,a} = -1.08$.

$[Bu^n_4N][Re_2Cl_6(dppp)]$ (3). Method 1. To a mixture of $[Bu^n_4N]_2[Re_2Cl_8]$ (0.115 g, 0.1 mmol) and dppp (0.247 g, 0.6 mmol) was added 30 mL of toluene. The mixture was refluxed for 4 days to give a grass-green solid and a green-brown solution. The solid was separated by filtration, washed on the frit with hexanes, dried, and then dissolved in 7 mL of CH_2Cl_2. The solution was layered with 12 mL of hexanes to yield dark-green crystals of $\alpha\text{-}Re_2Cl_4(dppp)_2\cdot 4CH_2Cl_2$.[10] Yield: 0.091

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[9] Crystal data for 1,3,6-$Re_2Cl_5(PPr^n_3)_3$: trigonal, $P3_1$ (No. 144), $a = 11.0686(4)$ Å, $c = 28.069(4)$ Å, $V = 2978.1(5)$ Å^3, $Z = 3$, $\rho_{calcd} = 1.723$ g/cm^3, $T = 213$ K, full matrix refinement on F^2 (Nonius FAST area detector, SHELXL-93), R1 (on F_o) = 0.0496, wR2 (on F_o^2) = 0.1305, GOF = 1.052, the Flack parameter $x = 0.01(2)$ for 351 parameters and 38 restraints, 4714 unique data (4608 with $I > 2\sigma(I)$). Re−Re = 2.2284(9) Å. Percentage occupancies for the Re_2 unit disorder 90.0, 7.9, and 2.1. See Supporting Information for other structure details.

Table 1. Crystallographic Data for $[Bu^n_4N][1,7\text{-}Re_2Cl_6(PPr^n_3)_2]$ (**1a**), $[Bu^n_4N][1,6\text{-}Re_2Cl_6(PPr^n_3)_2]$ (**1b**), $[Bu^n_4N][1,7\text{-}Re_2Cl_6(PEt_2Ph)_2]$ (**2**), and $[Bu^n_4N][Re_2Cl_6(\eta^2\text{-dppp})]$ (**3**)

	1a	1b	2	3
formula	$Re_2P_2NCl_6C_{34}H_{78}$	$Re_2P_2NCl_6C_{34}H_{78}$	$Re_2P_2NCl_6C_{36}H_{66}$	$Re_2P_2NCl_6C_{43}H_{62}$
fw	1148.01	1148.01	1159.94	1239.98
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	12.758(1)	16.3355(8)	11.868(1)	11.8986(4)
b, Å	15.755(5)	12.656(1)	12.125(2)	11.913(1)
c, Å	24.160(3)	22.892(2)	15.375(3)	18.383(2)
α, deg			88.01(1)	102.23(2)
β, deg	104.22(1)	94.735(6)	82.64(1)	108.003(5)
γ, deg			88.47(1)	97.38(1)
V, Å^3	4707(2)	4716.6(6)	2192.4(6)	2368.6(3)
Z	4	4	2	2
ρ_{calcd}, g·cm^{-3}	1.620	1.617	1.757	1.739
μ, mm^{-1}	5.570	5.559	5.981	5.543
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	−60	−60	−100	−60
transmission factors		0.324−0.574	0.6469−0.9989	
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0341, 0.0753	0.0451, 0.0970	0.0247, 0.0646	0.0388, 0.0965
R1,[a] wR2[b] (all data)	0.0407, 0.0803	0.0499, 0.1007	0.0301, 0.0671	0.0446, 0.1027

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

g (54%). The solvent was removed from the green-brown solution under reduced pressure to afford an oily residue. It was washed with hexanes vigorously, dried, and then dissolved in 8 mL of CH_2Cl_2. The dichloromethane solution was layered with 15 mL of hexanes to give brown crystals of **3**. Yield: 0.020 g (ca. 15%).

Method 2. To a solution containing $[Bu^n_4N]_2[Re_2Cl_8]$ (0.111 g, 0.1 mmol) in 15 mL of acetonitrile was added 0.245 g (0.6 mmol) of dppp. Stirring was continued for 42 h at room temperature to give a green-brown solution. The solvent was removed to leave a green-brown residue, which was washed with 15 mL of hexanes, dried, and then dissolved in 15 mL of benzene. The solution was layered with hexanes to give a few crystals of **3** along with some brown unidentified oily product. Yield: <10% (not optimized). Anal. Calcd for $Re_2P_2NCl_6C_{43}H_{62}$: C, 41.65; H, 5.04. Found: C, 41.19; H, 5.00. For $[Re_2Cl_6(dppp)]^-$: ESR (CH_2Cl_2, 100 K) centered at 2319 G, $g = 2.15$; CV (CH_2Cl_2, 22 °C, V vs Ag/AgCl) $E_{1/2}(ox) = +0.39$.

X-ray Crystallographic Procedures. Single crystals of compounds **1a**, **1b**, **2**, and **3** were obtained as described above. In each case, a crystal of suitable quality was affixed to the end of a quartz fiber with grease in a cold nitrogen stream (−60 or −100 °C). X-ray diffraction experiments were carried out using one of the two fully automated diffractometers equipped with monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å), CAD-4S (**2**) and Nonius FAST area detector (**1a**, **1b**, **3**). Unit cell determination and data collection followed routine procedures and practices of this laboratory.[11] 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[12] and the SHELXL-93 programs[13] on a DEC Alpha running VMS. In each model, the hydrogen atoms were included in the structure factor calculations at idealized positions. Relevant crystallographic data for complexes **1a**, **1b**, **2**, and **3** are summarized in Table 1.

An orientational disorder was encountered for all structures, except **3**. For molecule **2** two equally occupied orientations were refined for all carbon atoms of diethylphosphine ligands and tetrabutylammonium cation. Some carbon atoms of PPr^n_3 and Bu^n_4N groups (**1a** and **1b**) were found to be disordered over two sites. The second pairs of rhenium atoms, i.e., the second orientations of the Re−Re units, were located in **1a** and **1b** and their site occupancy factors (sof) converged to 0.019 and 0.185, respectively. For **1b** another set of chloride ligands corresponding to the second orientation of the metal−metal vector was also refined.

Results and Discussion

Synthetic Aspects. All new compounds described in this work contain the dirhenium(II,III) anions $[Re_2Cl_6P_2]^-$ ($P_2 = (PPr^n_3)_2$ (**1**), $(PEt_2Ph)_2$ (**2**), dppp (**3**)) and are kinetic products in the reaction of $[Re_2Cl_8]^{2-}$ with an appropriate phosphine ligand. Complete two-electron reduction leading to dirhenium(II,II) species $[Re_2Cl_4P_4]$[14] requires higher temperatures and/or prolonged reaction times. Other one-electron-reduction products have been obtained previously under specific conditions for a number of phosphines, such as $Re_2Cl_5(PR_3)_3$ ($PR_3 = PMe_3$,[7b] PMe_2Ph,[4b] PPr^n_3,[4e] PCy_2H[15]), $[Re_2Cl_4(PR_3)_4]^+$ ($PR_3 = PMe_3$[4d]), and $[Re_2Cl_6(PR_3)_2]^-$ ($PR_3 = PEt_3$[4e]).

The reaction of PEt_2Ph with $[Re_2Cl_8]^{2-}$ in propanol at room temperature goes in exactly the same way as for PEt_3[4e] to give the $[Re_2Cl_6(PEt_2Ph)_2]^-$ (**2**) species in high yield. When the reaction is performed in benzene, the yield is lower in accord with the previous observation[4e] that, depending on the solvent used, a disproportionation process to Re_2^{5+} and Re^{4+} can be an alternative to a one-electron reduction of the Re_2^{6+} core.

The reaction between PPr^n_3 and $[Re_2Cl_8]^{2-}$ in propanol has been recently described by us[4e] to result in $Re_2Cl_5(PPr^n_3)_3$ as the only product. However, in the present work we crystallized out the latter complex (as a polymorph[9] different from either one seen before) in a mixture with $[Re_2Cl_6(PPr^n_3)_2]^-$ (**1**). Surprisingly, our attempts to obtain **1** by direct reaction in diethyl ether (eq 1) were unsuccessful. This fact suggests that the appearance of **1** may be a result of decomposition of some

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(10) Crystal data for $\alpha\text{-}Re_2Cl_4(dppp)_2\cdot 4CH_2Cl_2$; triclinic, $P\bar{1}$ (No. 2), $a = 11.830(3)$ Å, $b = 12.134(2)$ Å, $c = 12.356(2)$ Å, $\alpha = 83.41(1)°$, $\beta = 74.80(2)°$, $\gamma = 63.02(2)°$, $V = 1525.3(5)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.828$ g/cm^3, $T = 173$ K, full matrix refinement on F^2 (Enraf-Nonius CAD4, SHELXL-93), R1 (on F_o) = 0.0231, wR2 (on F_o^2) = 0.0599, GOF = 1.128 for 343 papameters, 6623 unique data (6413 with $I > 2\sigma(I)$). Re−Re = 2.2559(8) Å. See Supporting Information for other structural details.

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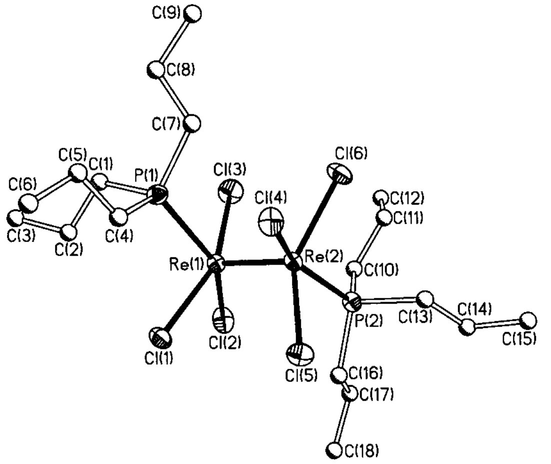


Figure 1. Perspective drawing of the $[1,7\text{-}Re_2Cl_6(PPr^n_3)_2]^-$ anion from **1a**. Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon atoms are shown as spheres of an arbitrary radius. Hydrogen atoms are omitted.

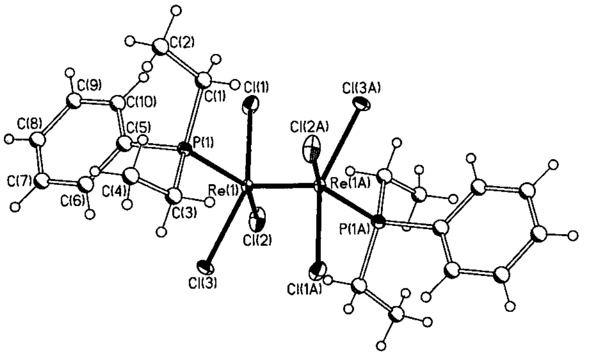


Figure 2. Perspective drawing of the $[1,7\text{-}Re_2Cl_6(PEt_2Ph)_2]^-$ anion from **2**. Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and hydrogen atoms are shown as spheres of arbitrary radii. Only one orientation of the diethylphenylphosphine ligand is depicted.

$$Re_2Cl_5(PPr^n_3)_3 + [Bu^n_4N]Cl \rightarrow [Bu^n_4N][Re_2Cl_6(PPr^n_3)_2] + PPr^n_3 \quad (1)$$

intermediate edge-sharing bioctahedral complex which is an initial product of the interaction between octachlorodirhenate and the phosphine. The transformation of such an intermediate compound depending on the solvent treatment has been mentioned by us for the case of PEt_3.[4e] It should be underlined here that based on the CV and the ESR spectrum there is only one conformation of the $[Re_2Cl_6(PPr^n_3)_2]^-$ in solution (at least at ambient temperatures), while in the solid state it crystallizes in two isomeric forms, namely, **1a** and **1b**.

The diphosphine complex containing the $[Re_2Cl_6(dppp)]^-$ anion (**3**) was isolated in low yield from the reaction of $[Re_2Cl_8]^{2-}$ with dppp in refluxing toluene or acetonitrile at room temperature. Complex **3** clearly is a kinetic product on the way to the dirhenium(II,II) compound $Re_2Cl_4(dppp)_2$. The latter was a major product of the reaction in toluene. It has been also obtained before[14b] when reaction in acetonitrile was performed under reflux conditions. We did not optimize the yield of **3**. In both cases the reaction mixtures were evidently complex with at least one more rhenium-containing paramagnetic compound present. This could be a mononuclear Re^{IV} complex, $ReCl_4(dppp)$, or the $Re^{II}-Re^{III}$ double-substituted species $[Re_2Cl_4(dppp)_2]^+$, depending on the reaction mechanism and the solvent used.

Table 2. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for $[Bu^n_4N][1,7\text{-}Re_2Cl_6(PPr^n_3)_2]$ (**1a**) and $[Bu^n_4N][1,6\text{-}Re_2Cl_6(PPr^n_3)_2]$ (**1b**)

	1a	**1b**
Re(1)−Re(2)	2.2141(4)	2.2211(6)
Re(1)−P(1)	2.409(2)	2.422(2)
Re(1)−Cl(1)	2.363(2)	2.364(5)
Re(1)−Cl(2)	2.377(2)	2.382(3)
Re(1)−Cl(3)	2.364(2)	2.332(3)
Re(2)−P(2)	2.422(2)	2.431(2)
Re(2)−Cl(4)	2.407(2)	2.396(7)
Re(2)−Cl(5)	2.354(2)	2.334(3)
Re(2)−Cl(6)	2.346(2)	2.377(3)
P(1)−Re(1)−Cl(1)	88.65(7)	87.2(2)
P(1)−Re(1)−Cl(2)	146.32(7)	157.2(1)
P(1)−Re(1)−Cl(3)	84.16(7)	84.47(9)
Cl(1)−Re(1)−Cl(2)	85.76(7)	86.9(2)
Cl(1)−Re(1)−Cl(3)	153.54(7)	141.6(2)
Cl(2)−Re(1)−Cl(3)	86.24(8)	86.6(1)
Re(2)−Re(1)−P(1)	98.18(5)	98.31(6)
Re(2)−Re(1)−Cl(1)	102.19(5)	112.7(1)
Re(2)−Re(1)−Cl(2)	115.47(5)	104.3(1)
Re(2)−Re(1)−Cl(3)	104.02(5)	105.58(9)
P(2)−Re(2)−Cl(4)	154.59(6)	88.4(2)
P(2)−Re(2)−Cl(5)	86.26(7)	84.20(9)
P(2)−Re(2)−Cl(6)	88.55(7)	155.0(1)
Cl(4)−Re(2)−Cl(5)	84.40(7)	144.2(2)
Cl(4)−Re(2)−Cl(6)	85.44(7)	85.5(2)
Cl(5)−Re(2)−Cl(6)	144.39(7)	86.6(1)
Re(1)−Re(2)−P(2)	94.88(5)	97.77(6)
Re(1)−Re(2)−Cl(4)	110.45(5)	110.8(2)
Re(1)−Re(2)−Cl(5)	107.22(5)	104.93(8)
Re(1)−Re(2)−Cl(6)	108.31(5)	107.05(9)
P(1)−Re(1)−Re(2)−Cl(4)	20.21(7)	15.6(2)
Cl(2)−Re(1)−Re(2)−Cl(5)		9.8(1)
Cl(2)−Re(1)−Re(2)−P(2)	16.70(7)	
Cl(1)−Re(2)−Re(1)−P(2)		16.5(2)
Cl(1)−Re(1)−Re(2)−Cl(5)	20.21(7)	
Cl(3)−Re(2)−Re(1)−Cl(6)	14.25(7)	10.5(1)
P(1)−Re(1)−Re(2)−P(2)	161.82(6)	106.89(8)

Molecular Structures. Compounds **1a** and **2** both contain the $1,7\text{-}Re_2Cl_6L_2$ type of structure with C_{2h} virtual symmetry, which is already well-known in the neutral form for $L = PMe_3$,[4a] PMe_2Ph,[4b] PEt_3,[8a−c] and $PMePh_2$,[8d] and has also recently been reported[4e] with $L = PEt_3$ in the monoanionic form. However, the structure of the latter has not been completely refined because of a twinning problem. The anions in the new compounds are shown in Figures 1 and 2, respectively. There are no unusual features in these structures. Bond distances and angles are given in Tables 2 and 3, respectively. In **1a**, there is a twist of about 18° away from a perfectly eclipsed conformation, while in **2** this distortion is very slight, about 1.5°.

The most novel result of this work is compound **1b**, which is the first $1,6\text{-}Re_2X_6L_2$ structure (Figure 3) ever seen. As mentioned before, in contrast to other pairs of $[Re_2X_{8-n}(PR_3)_n]$ isomers ($n = 3$ and 4), the 1,6 isomer of $[Re_2Cl_6(PPr^n_3)_2]^-$ (**1b**) can simply be obtained from $[1,7\text{-}Re_2Cl_6(PPr^n_3)_2]^-$ (**1a**) by a 90° rotation around the Re−Re vector without any ligand rearrangement required (Chart 1). Conversely, of course, the 1,6 isomer can readily revert to the 1,7 isomer simply by a 90° rotation. Presumably, the 1,7 isomer is the more stable one. In fact, the difference between the two isomers of the $[Re_2Cl_6(PPr^n_3)_2]^-$ ion is less than would be assumed from the idealized structures. There is a significant deviation (about 13°) from a perfectly eclipsed conformation in the structure of **1b** (Table 2), and repulsion between the PPr^n_3 ligands makes the P−Re−Re−P torsion angle 106.89(8)° rather than 90° (Figure 4b). Taking into account the deviation from perfect C_{2h} core

Table 3. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for $[Bu^n_4N][1,7\text{-}Re_2Cl_6(PEt_2Ph)_2]$ (**2**)

Re(1)−Re(1A)	2.2273(4)	Re(2)−Re(2A)	2.2278(5)
Re(1)−P(1)	2.389(1)	Re(2)−P(2)	2.404(1)
Re(1)−Cl(1)	2.348(1)	Re(2)−Cl(4)	2.361(1)
Re(1)−Cl(2)	2.380(1)	Re(2)−Cl(5)	2.384(1)
Re(1)−Cl(3)	2.359(1)	Re(2)−Cl(6)	2.355(1)
P(1)−Re(1)−Cl(1)	88.37(4)	P(2)−Re(2)−Cl(4)	86.83(4)
P(1)−Re(1)−Cl(2)	144.91(4)	P(2)−Re(2)−Cl(5)	146.07(4)
P(1)−Re(1)−Cl(3)	85.20(4)	P(2)−Re(2)−Cl(6)	87.21(4)
Cl(1)−Re(1)−Cl(2)	84.83(6)	Cl(4)−Re(2)−Cl(5)	84.61(5)
Cl(1)−Re(1)−Cl(3)	151.78(5)	Cl(4)−Re(2)−Cl(6)	151.49(4)
Cl(2)−Re(1)−Cl(3)	84.80(6)	Cl(5)−Re(2)−Cl(6)	84.92(5)
Re(1A)−Re(1)−P(1)	97.85(3)	Re(2A)−Re(2)−P(2)	97.69(3)
Re(1A)−Re(1)−Cl(1)	103.17(4)	Re(2A)−Re(2)−Cl(4)	104.49(3)
Re(1A)−Re(1)−Cl(2)	117.23(3)	Re(2A)−Re(2)−Cl(5)	116.24(4)
Re(1A)−Re(1)−Cl(3)	104.92(4)	Re(2A)−Re(2)−Cl(6)	103.93(3)
P(1)−Re(1)−Re(1A)−Cl(2A)	1.09(6)	P(2)−Re(2)−Re(2A)−Cl(5A)	−0.20(5)
Cl(1)−Re(1)−Re(1A)−Cl(3A)	2.76(5)	Cl(4)−Re(2)−Re(2A)−Cl(6A)	2.28(5)

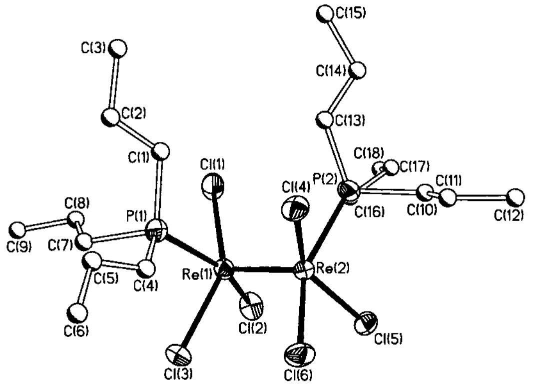


Figure 3. Perspective drawing of the $[1,6\text{-}Re_2Cl_6(PPr^n_3)_2]^-$ anion from **1b**. Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon atoms are shown as spheres of an arbitrary radius. Hydrogen atoms are omitted.

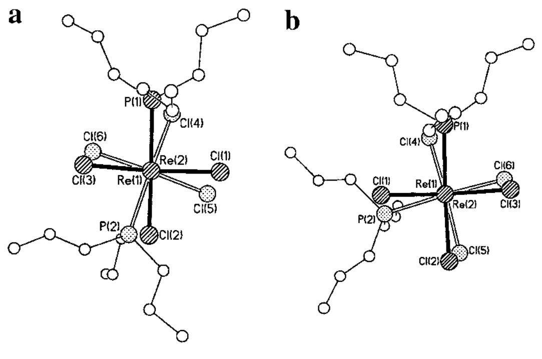


Figure 4. Views of the central part of molecules **1a** (a) and **1b** (b) directly down the Re−Re axis. Atoms are represented as spheres of arbitrary radii. Only rhenium and its neighboring atoms are labeled for clarity. For the torsion angles, see Table 2.

symmetry in **1a** (Figure 4a), where the P−Re−Re−P torsion angle is only 161.82(6)° instead of 180°, the actual difference between the two conformations in terms of torsion angle is only about 55° instead of 90°.

It should be noted that the structure of **1b** is chiral (having a C_2 axis as its only element of symmetry) and the unit cell contains two molecules of each chirality. Moreover, the anion of **1b** also shows the frequently observed disorder of the dirhenium unit (Chart 2) with a 0.815:0.185 ratio of the two orientations. Note that the two orientations are enantiomorphic. This is also one of the rare cases where the structure of the central unit is distorted enough and the occupancy of the minor orientation is high enough to allow the independent refinement of the second set of ligands corresponding to the second orientation.

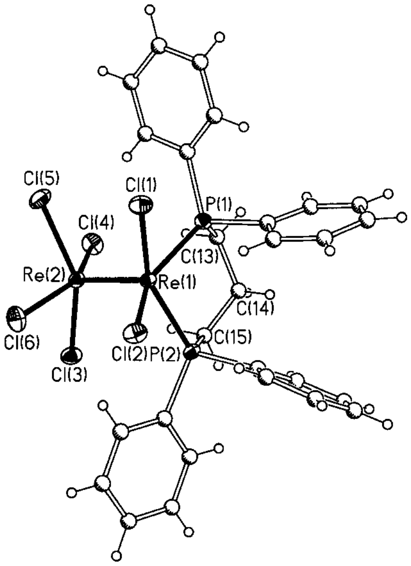
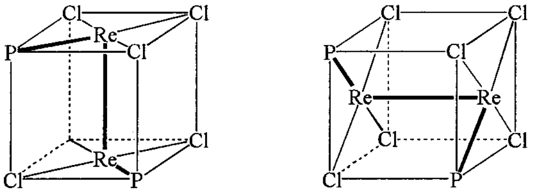


Figure 5. Perspective drawing of the $[Re_2Cl_6(\eta^2\text{-dppp})]^-$ anion in **3**. Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and hydrogen atoms are shown as spheres of arbitrary radii.

Chart 2



The structure of **3** is also interesting in several ways. It is just the second compound to have two more phosphorus atoms coordinated to one of the metal atoms than to the other one, as well as the second halide/phosphine dinuclear metal complex with only one diphosphine ligand (Figure 5). The first example was only recently found[16] with the tetrathiafulvalene phosphine ligand *o*-$\{PPh_2\}_2(CH_3)_2TTF$ (*o*-P2) in complex $[ReCl_2(o\text{-}P2)_2][Re_2Cl_6(o\text{-}P2)]$. Another example, α-$Re_2Cl_6$[(S,S)-diop] (diop = $Ph_2PCH_2CH(O)R$; R = $CHOCMe_2PPh_2CH_2$), has been obtained in solution,[17] but it converted upon crystallization to Re_2Cl_6[(S,S)-isodiop] where diphosphine ligand coordinates through P and O atoms.

The Re−Re bond in **3** has a length of 2.2458(5) Å (Table 4), which is slightly longer than those in molecules **1a**, **1b**, and **2**, but it is within the range of those known for the Re_2^{5+} core complexes.[2b] The dppp ligand is chelating on one rhenium atom with a typical P−Re−P angle of 88.87(7)°. It is also found that the Re−Cl bonds trans to the P atoms are about 0.05 Å longer than those on the other rhenium atom. This could be attributed to a trans influence by the phosphine ligands, but another explanation could be that the Re_2^{5+} core has a charge distribution that tends strongly toward $Re^{3+}-Re^{2+}$. The Re^{3+} attracts more of the negative ligands (Cl^-) and they approach it more closely because of the higher formal charge (3+), whereas the other

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(16) Uzelmeier, C. E.; Bartley, S. L.; Fourmigue, M.; Rogers, R.; Grandinetti, G.; Dunbar, K. R. *Inorg. Chem.* **1998**, *37*, 6706.

(17) Chen, J.-D.; Cotton, F. A. *J. Am. Chem. Soc.* **1991**, *113*, 2509.

Table 4. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for $[Bu^n_4N][Re_2Cl_6(\eta^2\text{-dppp})]$ (**3**)

Re(1)−Re(2)	2.2458(5)	Re(2)−Cl(3)	2.337(2)
Re(1)−P(1)	2.377(2)	Re(2)−Cl(4)	2.360(2)
Re(1)−P(2)	2.395(2)	Re(2)−Cl(5)	2.320(2)
Re(1)−Cl(1)	2.387(2)	Re(2)−Cl(6)	2.322(2)
Re(1)−Cl(2)	2.380(2)		
P(1)−Re(1)−P(2)	88.87(7)	Cl(3)−Re(2)−Cl(4)	82.61(8)
P(1)−Re(1)−Cl(1)	82.63(7)	Cl(3)−Re(2)−Cl(5)	147.98(8)
P(1)−Re(1)−Cl(2)	146.15(7)	Cl(3)−Re(2)−Cl(6)	86.44(8)
P(2)−Re(1)−Cl(1)	154.92(7)	Cl(4)−Re(2)−Cl(5)	86.33(9)
P(2)−Re(1)−Cl(2)	91.44(7)	Cl(4)−Re(2)−Cl(6)	148.09(8)
Cl(1)−Re(1)−Cl(2)	82.93(7)	Cl(5)−Re(2)−Cl(6)	87.32(9)
Re(2)−Re(1)−P(1)	102.36(5)	Re(1)−Re(2)−Cl(3)	111.09(5)
Re(2)−Re(1)−P(2)	97.83(5)	Re(1)−Re(2)−Cl(4)	112.84(6)
Re(2)−Re(1)−Cl(1)	107.02(5)	Re(1)−Re(2)−Cl(5)	100.90(6)
Re(2)−Re(1)−Cl(2)	111.11(6)	Re(1)−Re(2)−Cl(6)	99.07(6)
P(1)−Re(1)−Re(2)−Cl(4)	14.8(1)	Cl(1)−Re(1)−Re(2)−Cl(5)	10.2(1)
P(2)−Re(1)−Re(2)−Cl(3)	15.0(1)	Cl(2)−Re(1)−Re(2)−Cl(6)	10.1(1)

rhenium atom is formally 2+ and thus has a larger single-bond radius. The two possible explanations are complementary.

Concluding Remarks

This report describes our recent success in the isolation of three different types of isomers for mixed chloride/phosphine molecules having a dirhenium core of the composition $[Re_2Cl_6P_2]$. The structure of **1b** presented here is, in fact, the first one of its type ever seen for any M_2^{n+} core. We have found that a compound of the $[Re_2Cl_6(PR_3)_2]$ stoichiometry can crystallize not only as the well-known centrosymmetric C_{2h} isomer, but also as the noncentrosymmetric C_2 isomer. Therefore, in the future any allusion to a $M_2X_6L_2$ species will require the specification prefix (1,7 or 1,6) in order to state the arrangement of L ligands in the molecule.

The complex $[Re_2Cl_6(dppp)]^-$ (**3**), in which only one diphosphine ligand chelates on one of the metal atoms, is an example of a geometry which is possible for bidentate phosphines but not so far available for monodentate ones. This isomer is an intermediate on the way to the triply bonded bis-chelating type of complex, α-Re_2Cl_4(diphosphine)$_2$, and ultimately its β isomer. Another possible isomer of the stoichiometry $[Re_2Cl_6(\mu$-diphosphine)] which might be a direct precursor to the β-Re_2Cl_4(diphosphine)$_2$ species is still to be found. Also still missing is a 1,3-$Re_2Cl_6(PR_3)_2$ type of molecule or anion.

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

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