Further Studies of the Isomeric 1,2,7- and 1,3,6-$Re_2Cl_5(PMe_3)_3$ Compounds

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New studies of compounds containing $Re_2Cl_5(PMe_3)_3$ molecules have been carried out on products prepared by one-electron oxidation of Re(II)−Re(II) compounds as well as by one-electron reduction of Re(III)−Re(III) species. The action of $PhI{\cdot}Cl_2$ on $Re_2Cl_4(PMe_3)_4$ in 2:1 mole ratio, in the presence of free PMe_3, gives red 1,3,6-/1,2,7-$Re_2Cl_5(PMe_3)_3$ **(1)** containing two isomers in its unit cell. It was also shown that some additional 1,3,6-$Re_2Cl_5(PMe_3)_3$, isolated as its $^1/_2CH_2Cl_2$ solvate **(2)**, is always present in the reaction product. The reaction of the quadruply bonded complex $[(n\text{-}Bu)_4N]_2Re_2Cl_8$ with PMe_3 in propanol at room temperature leads to 1,2,7-$Re_2Cl_5(PMe_3)_3{\cdot}(n\text{-}Bu)_4NCl$ **(3)**. Heating a dichloromethane solution of compound **3** results in pure 1,2,7-$Re_2Cl_5(PMe_3)_3$. All molecules are characterized by a Re_2^{5+} core with a $\sigma^2\pi^4\delta^2\delta^*$ bond of order 3.5 and Re−Re distances within the range 2.210−2.227 Å. Crystal data are as follows: for **1**, monoclinic space group $P2_1/c$, $a = 14.936(5)$ Å, $b = 8.8206(8)$ Å, $c = 34.29(1)$ Å, $\beta = 90.77(2)°$, $V = 4517(2)$ Å^3, $Z = 8$; for **2**, monoclinic space group $P2_1/n$, $a = 8.907(1)$ Å, $b = 16.112(1)$ Å, $c = 16.683(3)$ Å, $\beta = 94.751(6)°$, $V = 2385.9(5)$ Å^3, $Z = 4$; for **3**, triclinic space group $P1$, $a = 8.911(2)$ Å, $b = 10.686(2)$ Å, $c = 10.979(3)$ Å, $\alpha = 101.12(2)°$, $\beta = 106.82(2)°$, $\gamma = 91.29(2)°$, $V = 978.5(4)$ Å^3, $Z = 1$.

Introduction

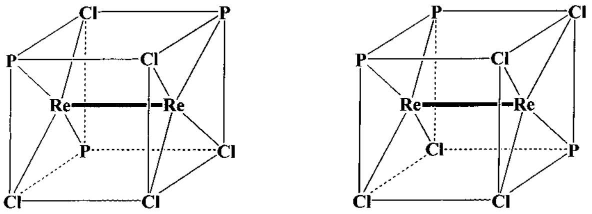
The title compounds have the structures shown in Figure 1. It is already well known[1] that they can be made[2] by treatment of $Re_2Cl_4(PMe_3)_4$ with Cl_2 (or $PhI{\cdot}Cl_2$). In the absence of excess PMe_3 the 1,3,6-isomer is obtained, while in the presence of about 1 molar equiv of added PMe_3 the 1,2,7-isomer is produced. There has been no explanation for the latter result, but since the 1,3,6-isomer would be expected to be more stable and is the only one ever seen with other phosphines (e.g., PEt_3), it is to be presumed that the formation of the 1,2,7-isomer is due to a kinetic (mechanistic) influence by the excess PMe_3.

In this paper we report some new results, with several novel features, obtained in further studies of the reaction leading to the 1,2,7-isomer. In one case, we obtained a crystalline product that contains both isomers in the same unit cell, a substance we designate 1,3,6-/1,2,7-$Re_2Cl_5(PMe_3)_3$ **(1)**. We have also obtained the 1,2,7-isomer by a new reaction which gives it initially in the unusual form of crystalline 1,2,7-$Re_2Cl_5(PMe_3)_3{\cdot}(n\text{-}Bu)_4NCl$ **(3)**.

Experimental Section

Starting Materials. General literature methods were used to prepare $Re_2Cl_4(PMe_3)_4$,[3,4] $[(n\text{-}Bu)_4N]_2Re_2Cl_8$,[5] and $PhI{\cdot}Cl_2$.[6] PMe_3 was purchased from Strem Chemicals. Common solvents were obtained from commercial sources and were dried and deoxygenated by refluxing over appropriate reagents before use. All manipulations were carried out under a nitrogen or an argon atmosphere by using standard vacuum-line techniques.

Syntheses. (i) 1,3,6-/1,2,7-$Re_2Cl_5(PMe_3)_3$ (1). A solution containing 0.1 g of $Re_2Cl_4(PMe_3)_4$, 30 μL of PMe_3, and 6 mL of dichloromethane was stirred at room temperature for 15 min. An excess of $PhI{\cdot}Cl_2$ (0.08 g) was added to the solution. A white powder (PMe_3Cl_2 or Me_3PO?) immediately precipitated, and the solution gradually turned brown. The mixture was left to stir at room temperature for 12 h, after which it was filtered. The solvent was then removed from the filtrate by vacuum distillation to leave a brown residue. This was redissolved in 5 mL of dichloromethane, and the solution was carefully layered with 5 mL of isomeric hexanes. After 1 week, large, red, needle-shaped crystals of **1** grew on the walls of the Schlenk tube; yield 0.06 g (63%).



1,3,6- (trans-)   1,2,7- (cis-)

Figure 1. 1,3,6- (trans-) and 1,2,7- (cis-) isomers in the compounds containing molecules of the $Re_2Cl_5(PMe_3)_3$ type.

(ii) 1,3,6-$Re_2Cl_5(PMe_3)_3{\cdot}{}^1/_2CH_2Cl_2$ (2). The compound 1,3,6-$Re_2Cl_5(PMe_3)_3{\cdot}{}^1/_2CH_2Cl_2$ was obtained when a dichloromethane solution of **1** was kept at about 40 °C overnight. It was then observed that a small amount of green, platelike crystals of compound **2** were always present in the solid product of reaction (i) together with the main product, **1**.

(iii) 1,2,7-$Re_2Cl_5(PMe_3)_3{\cdot}(n\text{-}Bu)_4NCl$ (3). $[(n\text{-}Bu)_4N]_2Re_2Cl_8$ (0.10 g) was added to a mixture of *n*-propyl alcohol (8 mL) and trimethylphosphine (1 mL). The reaction mixture was stirred at room temperature for 12 h, resulting in a brown solution. The solvent and the excess phosphine were then removed by vacuum distillation to leave a brown residue. This was dissolved in 5 mL of dichloromethane, the red-brown solution was filtered, and the filtrate was layered with isomeric hexanes. After a few days, dark red, block-shaped crystals of **3** were found on the bottom of the Schlenk tube; yield 0.08 g (86%).

Refluxing a dichloromethane solution of **3** for 24 h and then cooling effected a nearly quantitative conversion to the pure 1,2,7-$Re_2Cl_5(PMe_3)_3$[2] compound, which crystallized out.

Physical Measurements. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-

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Table 1. Crystallographic Data for 1,3,6-/1,2,7-$Re_2Cl_5(PMe_3)_3$ (**1**), 1,3,6-$Re_2Cl_5(PMe_3)_3 \cdot {}^1/_2CH_2Cl_2$ (**2**), and 1,2,7-$Re_2Cl_5(PMe_3)_3 \cdot (n\text{-}Bu)_4NCl$ (**3**)

formula	$Re_2Cl_5P_3$-C_9H_{27}	$Re_2Cl_6P_3$-$C_{9.5}H_{28}$	$Re_2Cl_6P_3$-$NC_{25}H_{63}$
fw	777.87	820.33	1055.77
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P1$ (No. 1)
a, Å	14.936(5)	8.907(1)	8.911(2)
b, Å	8.8206(8)	16.112(1)	10.686(2)
c, Å	34.29(1)	16.683(3)	10.979(3)
α, deg			101.12(2)
β, deg	90.77(2)	94.751(6)	106.82(2)
γ, deg			91.29(2)
V, $Å^3$	4517(2)	2385.9(5)	978.5(4)
Z	8	4	1
ρ_{calc}, g/cm^3	2.288	2.284	1.792
μ, mm^{-1}	11.501	11.002	6.729
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, °C	20 ± 2	20 ± 2	20 ± 2
transm factors	1.00−0.79	1.00−0.36	1.00−0.52
final *R* indices [$I > 2\sigma(I)$]: R1,[a] wR2[b]	0.045, 0.116	0.049, 0.132	0.057, 0.139
R indices (all data): R1,[a] wR2[b]	0.071, 0.154	0.072, 0.148	0.061, 0.144
quality-of-fit indicator[c]	1.072	1.058	1.125

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] Quality-of-fit $= [\sum[w(F_o^2 - F_c^2)^2]/(N_{observns} - N_{params})]^{1/2}$; based on all data.

n-butylammonium hexafluorophosphate (n-Bu_4NPF_6) 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 silver/silver chloride (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. X-Band ESR spectra of dichloromethane solutions were recorded at 10 K with a frequency of 9.4 GHz on a Bruker ESP 300 spectrometer.

X-ray Crystallographic Procedures. Crystallographic data for 1,3,6-/1,2,7-$Re_2Cl_5(PMe_3)_3$ **(1)**, 1,3,6-$Re_2Cl_5(PMe_3)_3 \cdot {}^1/_2CH_2Cl_2$ **(2)**, and 1,2,7-$Re_2Cl_5(PMe_3)_3 \cdot (n\text{-}Bu)_4NCl$ **(3)** were obtained using general procedures that have been fully described elsewhere.[7] Intensity data were collected at ambient temperature on an Enraf-Nonius CAD-4 diffractometer by using graphite-monochromated Mo Kα (λ_α = 0.710 73 Å) radiation. All calculations were performed on a DEC 3000-800 AXP workstation. Data were corrected for Lorentz and polarization effects. The coordinates of Re atoms in each case were obtained by Patterson and direct methods in SHELXS-86.[8] Final least-squares refinement for each structure was performed using the SHELXL-93 structure refinement program.[9] Crystallographic parameters and basic information pertaining to data collection and structure refinement are summarized in Table 1. Listings of positional and isotropic thermal parameters for compounds **1**−**3** will be found in the Supporting Information. Selected bond distances and angles are listed in Tables 2−4, and the atom-numbering schemes are defined in Figure 2. Tables of anisotropic displacement parameters as well as complete tables of bond distances and angles and coordinates of hydrogen atoms are available as Supporting Information.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1,3,6-/1,2,7- $Re_2Cl_5(PMe_3)_3$ (**1**)

Re(1)−Re(2)	2.2183(8)	Re(3)−Cl(6)	2.376(3)
Re(1)−Cl(2)	2.331(3)	Re(3)−P(5)	2.385(3)
Re(1)−Cl(1)	2.341(3)	Re(3)−Cl(7)	2.391(3)
Re(1)−P(1)	2.437(3)	Re(3)−P(4)	2.397(3)
Re(1)−P(2)	2.449(3)	Re(4)−Cl(10)	2.303(3)
Re(2)−Cl(3)	2.329(3)	Re(4)−Cl(9)	2.339(3)
Re(2)−Cl(4)	2.331(3)	Re(4)−Cl(8)	2.363(3)
Re(2)−Cl(5)	2.386(3)	Re(4)−P(6)	2.428(3)
Re(2)−P(3)	2.427(3)	Re(5)−Re(6)	2.23(3)
Re(3)−Re(4)	2.2261(5)	P−C(av)	1.81(1)

Re(2)−Re(1)−Cl(1)	115.30(8)	Re(4)−Re(3)−Cl(7)	108.24(8)
Re(2)−Re(1)−Cl(2)	108.67(8)	Re(4)−Re(3)−P(4)	98.00(7)
Re(2)−Re(1)−P(1)	100.55(8)	Re(4)−Re(3)−P(5)	98.11(7)
Re(2)−Re(1)−P(2)	103.05(9)	Cl(6)−Re(3)−Cl(7)	82.7(1)
Cl(1)−Re(1)−Cl(2)	136.0(1)	Cl(6)−Re(3)−P(4)	144.6(1)
Cl(1)−Re(1)−P(1)	87.7(1)	Cl(6)−Re(3)−P(5)	82.4(1)
Cl(1)−Re(1)−P(2)	86.7(1)	Cl(7)−Re(3)−P(4)	82.3(1)
Cl(2)−Re(1)−P(1)	84.0(1)	Cl(7)−Re(3)−P(5)	153.4(1)
Cl(2)−Re(1)−P(2)	83.8(1)	P(4)−Re(3)−P(5)	97.6(1)
P(1)−Re(1)−P(2)	155.9(1)	Re(3)−Re(4)−Cl(8)	111.85(7)
Re(1)−Re(2)−Cl(3)	110.68(8)	Re(3)−Re(4)−Cl(9)	112.37(8)
Re(1)−Re(2)−Cl(4)	110.71(9)	Re(3)−Re(4)−Cl(10)	102.04(8)
Re(1)−Re(2)−Cl(5)	104.35(8)	Re(3)−Re(4)−P(6)	95.91(7)
Re(1)−Re(2)−P(3)	98.82(7)	Cl(8)−Re(4)−Cl(9)	86.3(1)
Cl(3)−Re(2)−Cl(4)	138.3(1)	Cl(8)−Re(4)−Cl(10)	88.7(1)
Cl(3)−Re(2)−Cl(5)	86.6(1)	Cl(8)−Re(4)−P(6)	152.2(1)
Cl(3)−Re(2)−P(3)	83.8(1)	Cl(9)−Re(4)−Cl(10)	144.6(1)
Cl(4)−Re(2)−Cl(5)	87.8(1)	Cl(9)−Re(4)−P(6)	84.2(1)
Cl(4)−Re(2)−P(3)	85.4(1)	Cl(10)−Re(4)−P(6)	84.1(1)
Cl(5)−Re(2)−P(3)	156.8(1)	C−P−C(av)	103.4(6)
Re(4)−Re(3)−Cl(6)	117.15(8)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 1,3,6-$Re_2Cl_5(PMe_3)_3 \cdot {}^1/_2CH_2Cl_2$ (**2**)

Re(1)−Re(2)	2.211(1)	Re(2)−Cl(4)	2.336(4)
Re(1)−Cl(1)	2.368(4)	Re(2)−Cl(5)	2.347(3)
Re(1)−Cl(2)	2.430(4)	Re(2)−P(3)	2.461(4)
Re(1)−P(1)	2.442(4)	Re(3)−Re(4)	2.210(2)
Re(1)−P(2)	2.392(4)	P−C(av)	1.79(2)
Re(2)−Cl(3)	2.378(4)	C(10)−Cl(6)(av)	1.70(3)

Re(2)−Re(1)−Cl(1)	112.4(1)	Re(1)−Re(2)−Cl(4)	106.6(1)
Re(2)−Re(1)−Cl(2)	102.8(1)	Re(1)−Re(2)−Cl(5)	104.26(9)
Re(2)−Re(1)−P(1)	103.7(1)	Re(1)−Re(2)−P(3)	98.12(9)
Re(2)−Re(1)−P(2)	103.13(9)	Cl(3)−Re(2)−Cl(4)	147.4(2)
Cl(1)−Re(1)−Cl(2)	144.7(2)	Cl(3)−Re(2)−Cl(5)	87.7(2)
Cl(1)−Re(1)−P(1)	85.9(2)	Cl(3)−Re(2)−P(3)	82.7(2)
Cl(1)−Re(1)−P(2)	90.5(2)	Cl(4)−Re(2)−Cl(5)	87.9(1)
Cl(2)−Re(1)−P(1)	84.9(2)	Cl(4)−Re(2)−P(3)	89.1(2)
Cl(2)−Re(1)−P(2)	82.3(2)	Cl(5)−Re(2)−P(3)	157.3(1)
P(1)−Re(1)−P(2)	152.2(1)	C−P−C(av)	104(1)
Re(1)−Re(2)−Cl(3)	105.8(2)	Cl(6′)−C(10)−Cl(6)	112(3)

1,3,6-/1,2,7-$Re_2Cl_5(PMe_3)_3$ (1). A needle-shaped crystal with approximate dimensions 0.25 × 0.08 × 0.05 mm^3 was covered with a thin layer of epoxy resin and placed on the tip of a glass fiber. Cell parameters were obtained by indexing 25 reflections found randomly and refined by centering another 25 reflections in the range 26° ≤ 2θ ≤ 36°. Axial oscillation photographs were taken to confirm the Laue group (2/*m*) and the axial lengths. The ω−2θ scan method was used to collect a total of 8255 data in the range 4° ≤ 2θ ≤ 50°. Periodic monitoring of three representative reflections revealed no loss in crystal integrity throughout data collection. An absorption correction based on azimuthal scans of 6 reflections with the Eulerian angle χ near 90° was applied to the data. From the systematic absences the space group was uniquely assigned as $P2_1/c$ (No. 14).

The positions of four Re atoms were located using the direct-methods program in SHELXS-86. The chlorine, phosphorus, and carbon atoms were found from the subsequent least-squares refinements and difference Fourier maps. After anisotropic refinement, the second orientation of the Re−Re unit (Re(5) and Re(6)) in the 1,2,7-molecules was located. These atoms were included in the refinement, and their site occupancy factors (sof's) were allowed to vary against those of Re(3) and Re(4) but were constrained so that the sum for the Re atoms in the molecule equaled 2. The sof's converged to final values of 0.982 for Re(3), Re(4) and 0.018 for Re(5), Re(6). A total of 350 parameters were

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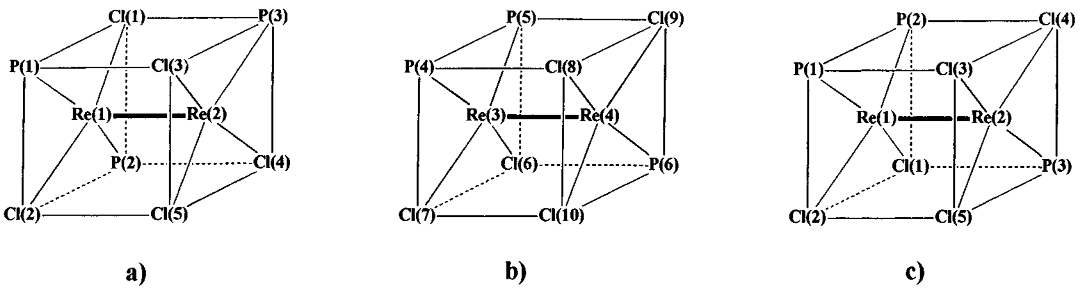

a) b) c)

Figure 2. Atom-numbering schemes for the 1,3,6-isomers from **1** and **2** (a), the 1,2,7-isomer from **1** (b), and the 1,2,7-isomer from **3** (c). Only Re$_2$ units and their coordination spheres are shown.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 1,2,7-Re$_2$Cl$_5$(PMe$_3$)$_3$·(n-Bu)$_4$NCl (**3**)

Re(1)−Re(2)	2.2274(8)	Re(2)−Cl(4)	2.337(5)
Re(1)−Cl(1)	2.395(5)	Re(2)−Cl(5)	2.307(6)
Re(1)−Cl(2)	2.382(5)	Re(2)−P(3)	2.430(5)
Re(1)−P(1)	2.397(5)	P−C(av)	1.81(2)
Re(1)−P(2)	2.386(6)	N(1)−C(av)	1.53(3)
Re(2)−Cl(3)	2.368(5)	C−C(av)	1.51(3)
Re(2)−Re(1)−Cl(1)	118.7(1)	Re(1)−Re(2)−Cl(5)	103.4(2)
Re(2)−Re(1)−Cl(2)	107.4(2)	Re(1)−Re(2)−P(3)	95.9(1)
Re(2)−Re(1)−P(1)	98.9(1)	Cl(3)−Re(2)−Cl(4)	86.2(2)
Re(2)−Re(1)−P(2)	96.9(2)	Cl(3)−Re(2)−Cl(5)	89.8(2)
Cl(1)−Re(1)−Cl(2)	82.9(2)	Cl(3)−Re(2)−P(3)	153.5(2)
Cl(1)−Re(1)−P(1)	142.2(2)	Cl(4)−Re(2)−Cl(5)	142.4(2)
Cl(1)−Re(1)−P(2)	84.2(2)	Cl(4)−Re(2)−P(3)	83.6(2)
Cl(2)−Re(1)−P(1)	81.7(2)	Cl(5)−Re(2)−P(3)	83.6(2)
Cl(2)−Re(1)−P(2)	155.6(2)	C−P−C(av)	103(1)
P(1)−Re(1)−P(2)	96.2(2)	C−N(1)−C(av)	110(2)
Re(1)−Re(2)−Cl(3)	110.6(2)	N(1)−C−C(av)	117(2)
Re(1)−Re(2)−Cl(4)	113.0(1)	C−C−C(av)	113(2)

varied in the final anisotropic refinement for all atoms except Re(5), Re(6), and hydrogen atoms of the methyl groups, to give $R = 0.045$ (for 6377 reflections with $I > 2\sigma(I)$) and $R = 0.071$ (for all 7926 data). The highest peak in the final difference map was 3.4 e/Å^3, lying 1.08 Å from the Re(2) atom.

1,3,6-Re$_2$Cl$_5$(PMe$_3$)$_3$·$^1/_2$CH$_2$Cl$_2$ (2). A plate-shaped crystal having dimensions 0.20 × 0.20 × 0.05 mm^3 was selected and glued to the tip of a glass fiber with epoxy cement. Least-squares refinement of 25 carefully centered reflections in the range $28° \le 2\theta \le 34°$ resulted in cell parameters consistent with a monoclinic lattice. From axial photographs and analysis of systematic absences, the space group was determined to be $P2_1/n$ (No. 14). A total of 3370 reflections in the range $4° \le 2\theta \le 45°$ were measured using the $\omega-2\theta$ scan technique. During data collection, no decay was observed. Azimuthal scans of 5 reflections were used for an empirical absorption correction.

The positions of four Re atoms, i.e., the main and one of the two possible secondary orientations, were determined from the Patterson map. During least-squares refinement the sof's of the two pairs of Re atoms (Re(1), Re(2) and Re(3), Re(4)) settled to values 0.617 and 0.383, respectively. Following least-squares refinements on the metal atom parameters, a difference Fourier map revealed the atoms of the coordination sphere of the Re$_2$ unit and also the Cl atoms of the dichloromethane molecule. Subsequent least-squares refinement and a difference Fourier map then showed carbon atoms of the PMe$_3$ ligands and also disordered C atoms in CH$_2$Cl$_2$ molecule. All non-hydrogen atoms were refined with anisotropic thermal parameters. Final least-squares refinement of 211 parameters resulted in $R = 0.049$ (for 2489 reflections with $I > 2\sigma(\mathrm{I})$) and $R = 0.072$ (for all 3137 data). The highest peak in the final difference map was 2.9 e/Å^3, lying 0.96 Å from a Re atom.

1,2,7-Re$_2$Cl$_5$(PMe$_3$)$_3$·(n-Bu)$_4$NCl (3). A blocklike crystal with dimensions 0.35 × 0.25 × 0.20 mm^3 was coated with epoxy cement and mounted on the tip of a glass fiber. Indexing based on 25 reflections with $12° \le 2\theta \le 25°$ resulted in a triclinic cell. The cell parameters were further refined on the basis of 25 reflections with 2θ from 32 to 38°. A total of 3688 reflections were collected by the ω scan technique. An empirical absorption correction was made on the basis of ψ-scans of 5 reflections.

A solution was initially made in the space group $P\bar{1}$ (No. 2), but without success by the refinement. In space group $P1$ (No. 1), a three-dimensional Patterson synthesis provided the positions of the two Re atoms. Subsequent alternating difference Fourier maps and least-squares refinements gave the positions of all non-hydrogen atoms. No metal−metal disorder was observed. Full refinement of 337 parameters led to residuals of $R = 0.057$ (for 3492 reflections with $I > 2\sigma(\mathrm{I})$) and $R = 0.061$ (for all 3686 reflections). The highest peak in the final difference map was 3.5 e/Å^3, lying 0.97 Å from the Re atom. The Flack parameter refined to 0.01(2) for the enantiomer chosen, thus confirming the choice for the crystal used. After several attempts, we have managed to pick up the crystal of another enantiomer and refined its structure.

Discussion

Chemical Aspects. The method by which the crystals of **1**, containing an equimolar mixture of the 1,3,6- and 1,2,7-isomers, were obtained is qualitatively very similar to the method previously used[2] to obtain the pure 1,2,7-isomer. However, the relative amounts of the of the reactants were different. The molar ratios associated with the reactions (two from ref 2 and the present reaction leading to **1**) are as follows:

Re$_2$Cl$_4$(PMe$_3$)$_4$	PMe$_3$	PhI·Cl$_2$	product	ref
1	0	1	1,3,6-isomer	2
1	1.25	1	1,2,7-isomer	2
1	2.50	2.40	1,3,6-/1,2,7- + some 1,3,6-isomer	this work

The preparation of compound **3** entails a type of reaction not previously observed, namely the use of a very basic phosphine, PMe$_3$, to attack [Re$_2$Cl$_8$]$^{2-}$ to yield a Re$_2$Cl$_5$(PMe$_3$)$_3$ product instead of Re$_2$Cl$_4$(PMe$_3$)$_4$. It was previously reported[3] that the reaction of PMe$_3$ with [(n-Bu)$_4$N]$_2$[Re$_2$Cl$_8$] in propanol yielded Re$_2$Cl$_4$(PMe$_3$)$_4$, but this was the product after a 10-day reflux. In the present work, the reaction was done at room temperature for only 0.5 day.

ref	[(n-Bu)$_4$N]$_2$Re$_2$Cl$_8$	PMe$_3$	1-propanol	conditions
3	0.20 g	1.0 mL	10 mL	10-day reflux
this work	0.10 g	1.0 mL	8 mL	12 h, room temp

We observed that, immediately after the addition of the phosphine to the suspension of [(n-Bu)$_4$N]$_2$Re$_2$Cl$_8$ in propanol, without heating, the reaction mixture turned brown. Its EPR spectrum (Figure 3) showed that some paramagnetic compound was present in solution. Evidently, even the most basic phosphines can provide the intermediate product if conditions are sufficiently mild. The real surprise, however, is that the isomer of Re$_2$Cl$_5$(PMe$_3$)$_3$ so formed is the 1,2,7- rather than 1,3,6-. Again, the question of kinetic versus thermodynamic control is raised, but in a reaction that proceeds by reduction of Re$_2$Cl$_6$(PMe$_3$)$_2$ rather than oxidation of Re$_2$Cl$_4$(PMe$_3$)$_4$.

Structural Aspects. Although all three compounds reported here consist of Re$_2$Cl$_5$(PMe$_3$)$_3$ molecules of known geometry

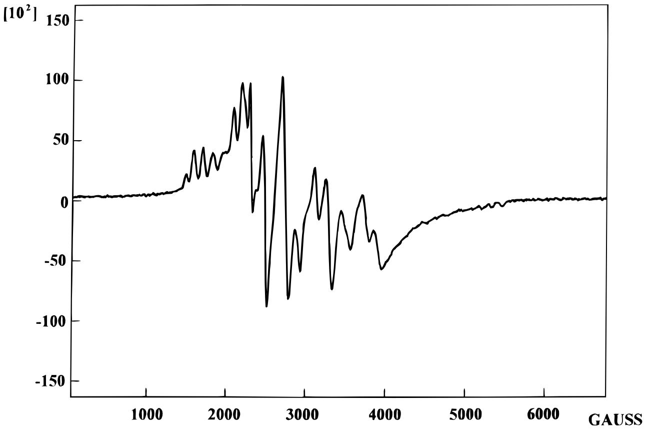

Figure 3. X-Band ESR spectrum in a frozen dichloromethane solution at 10 K for 1,2,7-$Re_2Cl_5(PMe_3)_3 \cdot (n\text{-}Bu)_4NCl$ **(3)**.

Table 5. Main Distances (Å) and Angles (deg) in $Re_2Cl_5(PMe_3)_3$ Molecules

1,3,6-$Re_2Cl_5(PMe_3)_3$	from ref 2	**2**	**1**
Re−Re′ [a]	2.218	2.211	2.2183
Re−Cl	2.340, 2.356	2.368, 2.430	2.331, 2.341
Re−P	2.425, 2.440	2.392, 2.442	2.437, 2.449
Re′−$Cl_{\text{trans to P}}$	2.373	2.347	2.368
Re′−Cl	2.324, 2.336	2.336, 2.378	2.329, 2.331
Re′−P	2.444	2.461	2.427
P−Re−P	154.7	152.2	155.9
1,2,7-$Re_2Cl_5(PMe_3)_3$	from ref 2	**1**	**3**
Re−Re′	2.226	2.2261	2.2274
Re−Cl	2.379, 2.401	2.376, 2.391	2.382, 2.395
Re−P	2.396, 2.400	2.385, 2.397	2.386, 2.397
Re′−$Cl_{\text{trans to P}}$	2.368	2.363	2.368
Re′−Cl	2.314, 2.338	2.303, 2.339	2.307, 2.337
Re′−P	2.435	2.428	2.430
P−Re−P	96.6	97.6	96.2

[a] Re atom coordinates two PMe_3 ligands; Re′ coordinates one PMe_3 ligand.

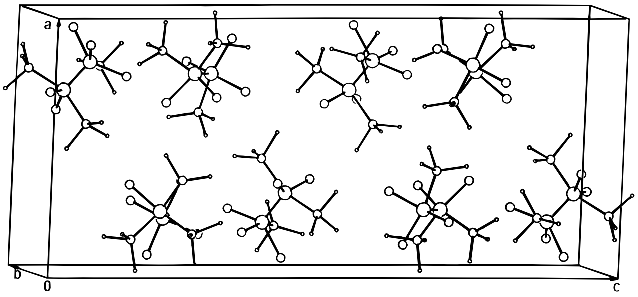

Figure 4. Packing diagram of 1,3,6-/1,2,7-$Re_2Cl_5(PMe_3)_3$ (1) showing 4 molecules of the 1,3,6-isomer and 4 molecules of the 1,2,7-isomer in the unit cell.

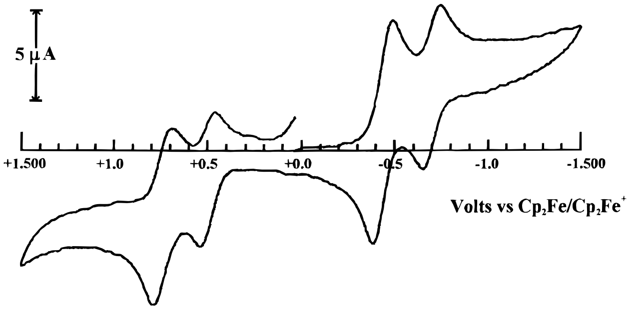

Figure 5. Cyclic voltammogram of 1,3,6-/1,2,7-$Re_2Cl_5(PMe_3)_3$ (1) in dichloromethane solution at room temperature. The half-wave potentials (V) are +0.52 (ox), +0.75 (ox) and −0.70 (red), −0.44 (red). The corresponding values (V) for pure 1,3,6-$Re_2Cl_5(PMe_3)_3$ and +0.46 (ox) and −0.75 (red)[2] and for pure 1,2,7-$Re_2Cl_5(PMe_3)_3$ are +0.68 (ox) and −0.48 (red).[2]

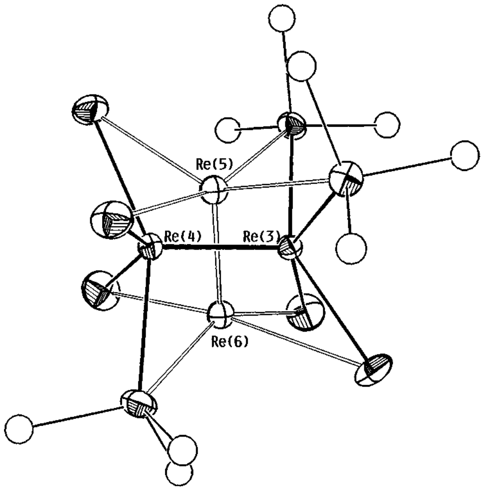

Figure 6. ORTEP drawing showing how the two orientations of the Re_2 unit in the 1,2,7-molecule of 1,3,6-/1,2,7-$Re_2Cl_5(PMe_3)_3$ (1) both conform to the same arrangement of ligands. Atoms are represented by thermal ellipsoids at the 50% probability level. Carbon atoms are shown as spheres of arbitrary radii.

Table 6. Orientational Disorder in $M_2Cl_5(PR_3)_3$ Type Molecules

complex	1st orientation	2nd orientation	3rd orientation	ref
1,3,6-$Re_2Cl_5(PMe_3)_3$	100.0	0.0	0.0	2
from **1**	100.0	0.0	0.0	this work
from **2**	61.7	38.3	0.0	this work
1,3,6-$Re_2Cl_5(PEt_3)_3$	64.2	32.1	3.7	2
1,3,6-$W_2Cl_5(PMe_3)_3$	98.2	1.8	0.0	11
1,3,6-$Tc_2Cl_5(PMe_2Ph)_3$	96.7	1.8	1.5	12
1,2,7-$Re_2Cl_5(PMe_3)_3$	100.0	0.0		2
from **1**	98.2	1.8		this work
from **3**	100.0	0.0		this work

(Table 5), each of them displays novel structure features. Compound **1** contains four molecules each of the 1,2,7- and 1,3,6-isomers that occupy alternating positions in its crystal structure (Figures 4 and 5). This presents an example of the rare situation in which two isomers cocrystallize. Another example in the realm of multiply-bonded dimetal compounds was reported a few years ago (cisoid and transoid $Mo_2(O_2CCF_3)_2Cl_2(NCC_2H_5)_2$[10]), but generally speaking, such crystals are uncommon. It is interesting to compare the partial volume for both isomeric molecules in compound **1** (1129 Å^3) with the sum of partial volumes per formula unit for pure[2] 1,3,6- and 1,2,7-complexes (1121 Å^3). This clearly indicates that there is no problem in mutual packing of different isomers in **1**. Another unexpected feature for this structure, illustrated in Figure 6, is a small disorder of the dimetal unit in both of the two possible orientations for 1,2,7-molecules. This was not observed for the pure 1,2,7-isomer[2] nor for this molecule in **3** (Table 6).

The formation of **2**, 1,3,6-$Re_2Cl_5(PMe_3)_3 \cdot {}^1/_2CH_2Cl_2$ (Figure 7), is a little surprising since 1,3,6-$Re_2Cl_5(PMe_3)_3$ was previously obtained from CH_2Cl_2 solution in a different crystal form containing no solvent of crystallization. The main difference in the crystal structures of these two forms is a disorder in two orientations of the Re_2 unit in compound **2** (Figure 8), whereas no disorder was found for the pure 1,3,6-isomer[2] (Table 6). The

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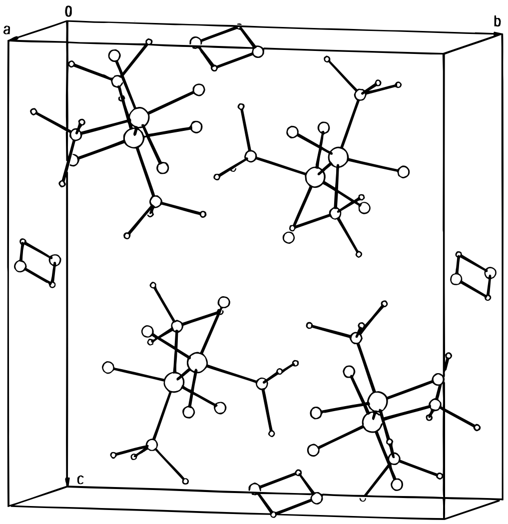

Figure 7. Packing diagram of 1,3,6-$Re_2Cl_5(PMe_3)_3\cdot{}^1/_2CH_2Cl_2$ (2). Only the major orientation of Re_2 units is shown.

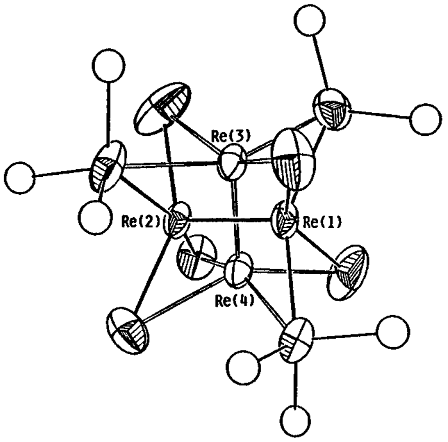

Figure 8. ORTEP diagram of the disordered Re_2 unit in 1,3,6-$Re_2Cl_5(PMe_3)_3\cdot{}^1/_2CH_2Cl_2$ (2) showing 50% probability ellipsoids. Carbon atoms are shown as spheres of arbitrary radii.

reason for that may be that molecules of dichloromethane separate molecules of the dimeric complex, resulting in no short contacts between the second Re−Re orientation and ligands of the neighboring 1,3,6-molecule.

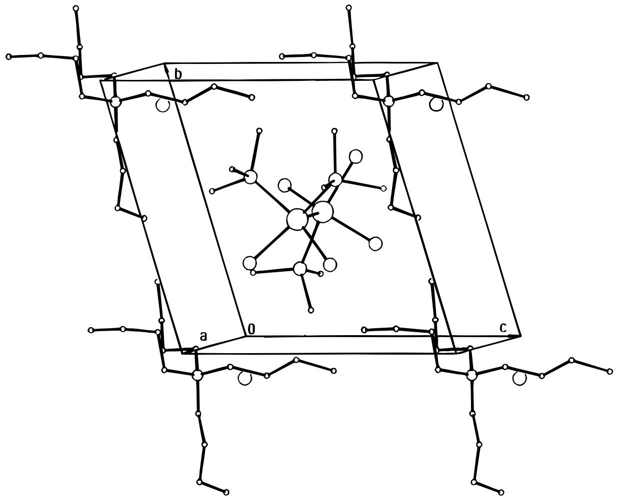

Figure 9. Packing diagram of 1,2,7-$Re_2Cl_5(PMe_3)_3\cdot(n\text{-Bu})_4NCl$ (3) showing the arrangement of $(n\text{-Bu})_4N^+$ cations and Cl^- anions around the 1,2,7-$Re_2Cl_5(PMe_3)_3$ molecule.

Compound **3** presents a case of cocrystallizing the 1,2,7-$Re_2Cl_5(PMe_3)_3$ isomer with tetrabutylammonium chloride. This, in itself, is rather unusual. Moreover, the unit cell contains only one asymmetric formula unit. It should be noted that we verified that the correct enantiomer was refined for the crystal used to collect data. It is interesting to note that the crystals of the pure 1,2,7-isomer[2] contained equal numbers of the two enantiomers. This is in accord with the usual behavior of racemic compounds, for which better packing is obtained when both enantiomers are present. What allows the separation of the enantiomers in the case of **3** is that the 1,2,7-$Re_2Cl_5(PMe_3)_3$ molecules are isolated from each other by the $(n\text{-Bu})_4N^+$ and Cl^- ions that lie between them (Figure 9). It may also be noted that interconversion of the enantiomeric molecules (1,2,7- and 1,2,8-) can occur easily by rotation about the Re−Re bond so that solutions of this geometric isomer, no matter how made or treated, will always be racemic.

Acknowledgment. We thank the National Science Foundation for support.

Supporting Information Available: Tables of crystal data and structure refinement parameters, complete bond lengths and angles, anisotropic displacement parameters, and all atomic coordinates and isotropic displacement parameters (23 pages). Ordering information is given on any current masthead page.

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