Mixed Chloride/Phosphine Complexes of the Dirhenium Core. 10. Redox Reactions of an Edge-Sharing Dirhenium(III) Non-metal−Metal-Bonded Complex, $Re_2(\mu\text{-}Cl)_2Cl_4(PMe_3)_4$

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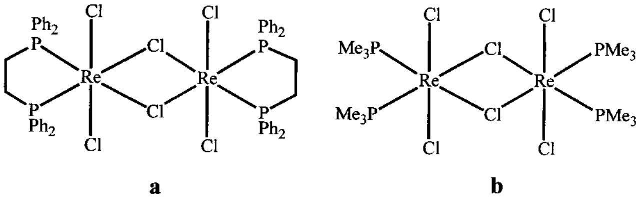
Reduction and oxidation reactions of the dirhenium(III) non-metal−metal-bonded edge-sharing complex, $Re_2(\mu\text{-}Cl)_2Cl_4(PMe_3)_4$ (**1**), have been studied. Several new mono- and dinuclear rhenium compounds have been isolated and structurally characterized in the course of this study. Reductions of **1** with 1 and 2 equiv of KC_8 result in an unusual face-sharing complex having an Re_2^{5+} core, $Re_2(\mu\text{-}Cl)_3Cl_2(PMe_3)_4$ (**2**), and a triply bonded Re^{II} compound, 1,2,7,8-$Re_2Cl_4(PMe_3)_4$ (**3**), respectively. Two-electron reduction of **1** in the presence of tetrabutylammonium chloride affords a new triply bonded complex of the Re_2^{4+} core, $[Bu^n_4N][1,2,7\text{-}Re_2Cl_5(PMe_3)_3]$ (**4**). Oxidation of **1** with $NOBF_4$ yields a Re^{IV} mononuclear compound, *trans*-$ReCl_4(PMe_3)_2$ (**5**). Two isomers of the monomeric Re^{III} anion, $[ReCl_4(PMe_3)_2]^-$ (**6**, **7**), have been isolated as side products. The crystal structures of compounds **2** and **4**−**7** have been determined by X-ray crystallography. The Re−Re distance in the face-sharing complex **2** of 2.686(1) Å is relatively short. The metal−metal bond length in anion **4** of 2.2354(7) Å is consistent with the usual values for the triply bonded Re_2^{4+} core compounds. In addition, a cis arrangement of trimethylphosphine ligands in the starting material **1** is retained upon reduction in the dinuclear products **2**−**4**.

Introduction

The chemistry of dirhenium(III) complexes in which there are multiple metal−metal bonds has been widely explored,[1] whereas in contrast, that of the compounds exhibiting no rhenium−rhenium bond is little known. For the latter, only two edge-sharing bioctahedral species have been known.[2,3] The complex $Re_2(\mu\text{-}Cl)_2Cl_4(dppe)_2$ (Chart 1a) with chelating diphosphine ligands was reported a long time ago.[3] Recently we have found[2] a synthetic route to obtain $Re_2(\mu\text{-}Cl)_2Cl_4(PMe_3)_4$ (**1**) (Chart 1b) as an intermediate on the way to the reduced chloride/phosphine dirhenium species. Complex **1** is an edge-sharing bioctahedral compound with two PMe_3 ligands having a cis disposition at each Re^{III} center and located in the same plane as the metal atoms and the bridging chloride ligands. The Re···Re distance of 3.85 Å in **1** indicates that there is no metal to metal bond in this molecule. Complex **1** is paramagnetic, but its electronic and redox properties are not well-understood. Electrochemical reduction and oxidation reactions of **1** were found by cyclic voltammetry to be irreversible. That means that species $[Re_2Cl_6(PMe_3)_4]^-$ and $[Re_2Cl_6(PMe_3)_4]^+$ are unstable and decompose or are transformed rapidly in solution. Therefore, investigation into the consequences of chemical addition and removal of electrons to and from the nonbonding dirhenium(III) system in **1** seemed of interest, as it could provide additional information on the stability and the reactivity of such compounds, and could allow us to find out what the irreversibly produced products are. Because of the unique characteristics of **1**, we hoped that by using it as a starting material under mild reaction conditions it would be possible to isolate compounds for which no direct synthetic routes were yet available. Indeed, reactions of reduction and oxidation of **1** accomplished in this work afforded several new rhenium compounds with oxidation states ranging from Re^{II} to Re^{IV}.

Chart 1



Reductions of **1** with 1 and 2 equiv of KC_8 result in the new face-sharing complex of the Re_2^{5+} core, $Re_2(\mu\text{-}Cl)_3Cl_2(PMe_3)_4$ (**2**), and the triply bonded Re^{II} compound, 1,2,7,8-$Re_2Cl_4(PMe_3)_4$ (**3**), which was recently obtained using a different approach.[2] The two-electron reduction of **1** in the presence of $[Bu^n_4N]Cl$ leads to a new triply bonded complex $[Bu^n_4N][Re_2Cl_5(PMe_3)_3]$ (**4**). All dirhenium complexes **2**−**4** have a cis coordination of trimethylphosphine ligands at the rhenium centers. Oxidation of **1** with 1 equiv of $NOBF_4$ yields a mononuclear rhenium(IV) product, *trans*-$ReCl_4(PMe_3)_2$ (**5**). Compound **5** is of the *trans*-$ReX_4(PR_3)_2$ (X = Cl, Br, I; PR_3 = tertiary phosphine) type, known for a long time,[1] but the crystal structure of the trimethylphosphine analogue has not yet been reported. Another monomeric rhenium(III) complex, $[Bu^n_4N]$[*trans*-$ReCl_4(PMe_3)_2$] (**6**), has been isolated as one of the products when oxidation was performed in the presence of $[Bu^n_4N]Cl$. Its isomeric [*cis*-$ReCl_4(PMe_3)_2]^-$ anion (**7**) has been obtained from the reduction

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of **1** with cobaltocene, which yielded complex **2** as the main product.

Experimental Section

General Procedures. All the syntheses and purifications were carried out under an atmosphere of N_2 in standard Schlenkware. All solvents used were freshly distilled under N_2 from suitable drying agents. Chemicals were purchased from the following commercial sources and used as received: $[Bu^n_4N]_2[Re_2Cl_8]$, $Co(C_5H_5)_2$, $NOBF_4$, Aldrich, Inc.; PMe_3, Strem Chemicals; dichloromethane-d_2, Cambridge Isotope Laboratories. A literature procedure[4] was used to prepare potassium-graphite, KC_8, by heating the two components under an N_2 atmosphere at 180−200 °C for about 1 h.

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. 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. Elemental analyses were done by Canadian Microanalytical Services, Ltd.

Synthetic Procedures. Preparation of 1,3,5,7-$Re_2Cl_6(PMe_3)_4$ (1). A suspension of $[Bu^n_4N]_2[Re_2Cl_8]$ (0.228 g, 0.200 mmol) in 15 mL of benzene was stirred for 5−6 h with an excess of PMe_3 (1 mL) at room temperature to give a pale-brown precipitate, containing the desired product **1** contaminated with tetrabutylammonium chloride (ratio is about 1:2). This solid was isolated by filtration, washed with hexanes (2 × 10 mL), and dried under vacuum. Yield: 0.204 g (71%).

The solid was then dissolved in 15 mL of CH_2Cl_2, and the solution was carefully layered with 20 mL of hexanes. The crystals of **1** started to grow in a few hours and were collected after 2 days. Yield: 0.062 g (35%). In a few more days all crystals disappeared due to decomposition processes at room temperature. Crystals of **1** (stable when solvent free) can be washed with water and cold ethanol to get rid of the traces of $[Bu^n_4N]Cl$. They were used for the syntheses of **2**, **3**, **5**, and **7**.

Reduction of 1 with 1 Equiv of KC_8. Crystals of **1** (0.090 g, 0.10 mmol) were mixed with KC_8 (0.018 g, 0.13 mmol) in an Ar glovebox, and then the mixture of solvents (6 mL of toluene and 3 mL of CH_2Cl_2) was added to the solids. The suspension was stirred for 2 h at room temperature. It was then filtered, and the green filtrate was layered with 15 mL of hexanes. Brownish plate-shaped crystals of $Re_2Cl_5(PMe_3)_4$ (**2**) came out in a few days. Yield: 0.055 g (64%). Anal. Calcd for $Re_2P_4Cl_5C_{12}H_{36}$ (**2**): C, 16.88; H, 4.26. Found: C, 16.93; H, 4.22. ESR (CH_2Cl_2, 100 K): centered at 3099 G, $g = 2.17$.

Reduction of 1 with 1 Equiv of $Co(\eta^5\text{-}C_5H_5)_2$. Crystals of **1** (0.090 g, 0.10 mmol) were dissolved in 10 mL of CH_2Cl_2, and cobaltocene (0.020 g, 0.10 mmol) was then added to the solution. After the mixture had been stirred for about 40 min at room temperature, the solvent was removed under reduced pressure. The resulting red-brown solid was dried in a vacuum and then dissolved in 7 mL of CH_2Cl_2. The dichloromethane solution was layered with 15 mL of hexanes. A few red crystals of $[Co(\eta^5\text{-}C_5H_5)_2][ReCl_4(PMe_3)_2]$ (**7**) appeared over a period of 2 weeks along with main product **2**. Yield of **7**: 0.020 g (15%).

Reduction of 1 with 2 Equiv of KC_8. Crystals of **1** (0.098 g, 0.11 mmol) were mixed with KC_8 (0.035 g, 0.26 mmol), and then 10 mL of toluene was added to the mixture. The suspension was stirred for 2 h at room temperature. The color of the solution turned greenish. The mixture was filtered, and the green filtrate was layered with 20 mL of hexanes. When the layers had mixed in a couple of days, the solution was placed in the freezer. Small green blocks of $Re_2Cl_4(PMe_3)_4$ (**3**) appeared in a few days. They were confirmed by NMR, CV, and X-ray diffraction study to be the 1,2,7,8-isomer of $Re_2Cl_4(PMe_3)_4$.[2] Yield: 0.061 g (67%).

Reduction of 1 with 2 Equiv of KC_8 in the Presence of $[Bu^n_4N]Cl$. A suspension of $[Bu^n_4N]_2[Re_2Cl_8]$ (0.220 g, 0.20 mmol) in 15 mL of benzene was stirred for 5−6 h with an excess of PMe_3 (1 mL) at room temperature to give a pale-brown precipitate, containing the desired product **1** contaminated with tetrabutylammonium chloride (ratio is about 1:2). This solid was isolated by filtration, washed with hexanes (2 × 10 mL) and dried under vacuum. This raw material was used for the synthesis of **4** (vide infra).

KC_8 (0.050 g, 0.38 mmol) was added to 0.204 g of the mixture (ca. 0.15 mmol of **1** with ca. 2 equiv of $[Bu^n_4N]Cl$) followed by 12 mL of toluene. The suspension was stirred for about 30 min at room temperature. The color of the solution immediately turned from red-brown to the greenish-brown. The mixture was filtered to remove the graphite and KCl, and the resulting brown-green toluene filtrate was layered with 15 mL of hexanes. Greenish-brown crystals of $[Bu^n_4N][Re_2Cl_5(PMe_3)_3]$ (**4**) came out in a few hours. Yield: 0.82 g (53%). Anal. Calcd for $Re_2P_3NCl_5C_{25}H_{63}$ (**4**): C, 29.43; H, 6.24. Found: C, 29.59; H, 6.18. CV (CH_2Cl_2, 22 °C, V vs Ag/AgCl): $E_{1/2}(ox)(1) = -0.46$, $E_{1/2}(ox)(2) = +0.73$.

Oxidation of 1 with $NOBF_4$. Crystals of **1** (0.132 g, 0.15 mmol) were mixed with $NOBF_4$ (0.024 g, 0.20 mmol); then 10 mL of CH_2Cl_2 was added to the mixture. The solution was stirred for about 2 h at room temperature, during which time the color turned intense red. The solution was layered with 10 mL of hexanes; after the layers mixed in 2 days, it was kept at −20 °C. Red crystals of $ReCl_4(PMe_3)_2$ (**5**) came out in 3 weeks. There was some unidentified blue-green crystalline material present in the mixture. Yield of **5**: 0.029 g (20%). Anal. Calcd for $ReP_2Cl_4C_6H_{18}$ (**5**): C, 15.01; H, 3.79. Found: C, 14.98; H, 3.89.

When the mixture of **1** with $[Bu^n_4N]Cl$ was used for reaction with $NOBF_4$, along with **5** a very few yellow crystals of $[Bu^n_4N][ReCl_4(PMe_3)_2]$ (**6**) have been found; they were separated manually. Yield: ca. 10%.

X-ray Crystallography. General Procedures. Single crystals of compounds **2**−**7** were obtained as described in the Experimental Section. X-ray diffraction studies of **2**−**7** were carried out on a Nonius FAST diffractometer with an area detector using Mo Kα radiation. Details for data collection have been fully described elsewhere.[5] In each case, a crystal of suitable quality was affixed to the end of a quartz fiber with grease in the cold nitrogen stream at −60 °C (−81 °C for **6**). Fifty reflections were used in cell indexing and about 250 reflections in cell refinement. Data were collected in the range $4° < 2\theta < 45°$ ($4° < 2\theta < 50°$ for **6**). Oscillation photographs of principal axes were taken to confirm Laue class and axial lengths. All data were corrected for Lorentz and polarization effects by the MADNES program.[6] The intensities for the crystals of **2**, **4**, and **7** were also corrected for anisotropy effects using a local adaptation of the program SORTAV.[7]

All calculations were done on a DEC Alpha running VMS. The coordinates of rhenium atoms for all of the structures were found in direct methods *E* maps using the structure solution program SHELXTL.[8] The positions of the remaining atoms were located by use of a combination of least squares refinements and difference Fourier maps in the SHELXL-93 program.[9] In all structures hydrogen atoms were included in the structure factor calculations at idealized positions.

Relevant crystallographic data for compounds **2** and **4**−**7** are presented in Table 1.

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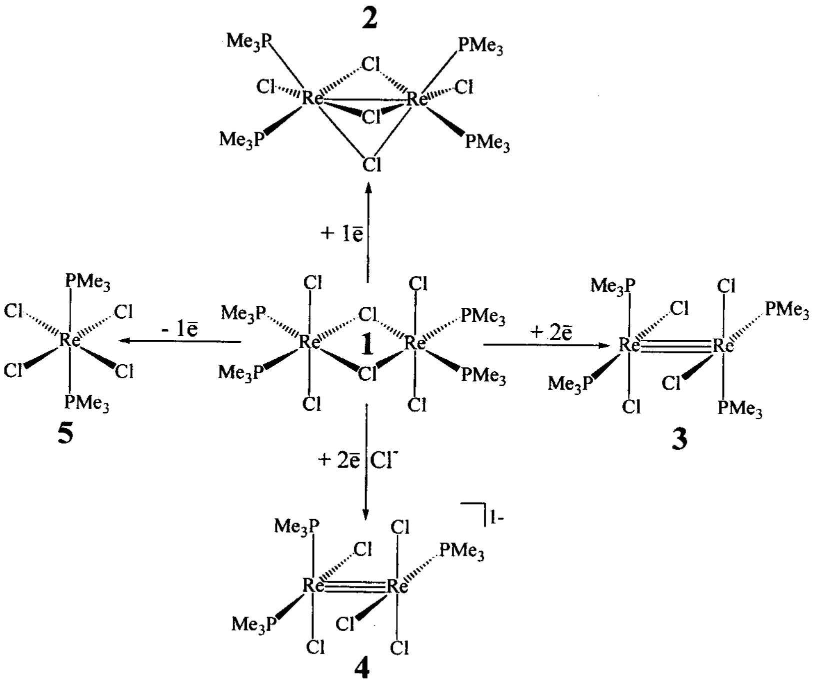
Table 1. Crystallographic Data for $Re_2(\mu\text{-}Cl)_3Cl_2(PMe_3)_4$ (**2**), $[Bu^n{}_4N][Re_2Cl_5(PMe_3)_3]$ (**4**), *trans*-$ReCl_4(PMe_3)_2$ (**5**), $[Bu^n{}_4N]$[*trans*-$ReCl_4(PMe_3)_2$] (**6**), and $[Co(\eta^5\text{-}C_5H_5)_2]$[*cis*-$ReCl_4(PMe_3)_2$] (**7**)

	2	**4**	**5**	**6**	**7**
formula	$Re_2P_4Cl_5C_{12}H_{36}$	$Re_2P_3Cl_5N_1C_{25}H_{63}$	$Re_1P_2Cl_4C_6H_{18}$	$Re_1P_2Cl_4N_1C_{22}H_{54}$	$Re_1P_2Cl_4Co_1C_{16}H_{28}$
fw, g mol^{-1}	853.94	1020.32	480.14	722.60	669.25
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	9.377(2)	9.561(2)	6.6010(7)	11.4415(9)	13.520(1)
b, Å	13.071(2)	21.812(3)	8.4258(9)	12.9675(5)	12.6811(8)
c, Å	10.818(2)	18.864(2)	13.4320(8)	21.9528(5)	14.055(1)
β, deg	94.65(2)	101.15(1)	100.71(1)	91.402(4)	97.567(7)
V, Å^3	1321.6(4)	3860(1)	734.1(1)	3256.1(3)	2388.7(3)
Z	2	4	2	4	4
ρ_{calcd}, g cm^{-3}	2.146	1.756	2.172	1.474	1.861
μ, mm^{-1}	9.896	6.753	9.185	4.169	6.337
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
transm factors	0.320−0.656	0.389−0.720			0.755−0.898
temp, °C	−60	−60	−60	−81	−60
data/obsd/params	2946/2895/208	5068/4012/324	946/781/61	5243/4577/264	3127/2788/217
R1^a, wR2^b[$I > 2\sigma(I)$]	0.0630 0.1625	0.0467 0.1215	0.0427 0.1160	0.0448 0.1108	0.0336 0.0767
R1^a, wR2^b(all data)	0.0637 0.1642	0.0606 0.1297	0.0486 0.1288	0.0524 0.1188	0.0403 0.0817
GOF	1.042	1.073	1.078	1.055	1.125

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

Scheme 1



Results and Discussion

Synthetic Aspects. The starting point for the chemistry described in this report is the dirhenium(III) non-metal−metal-bonded edge-sharing complex, $Re_2(\mu\text{-}Cl)_2Cl_4(PMe_3)_4$ (**1**), which was obtained recently[2] when we found a synthetic way to convert the quadruply bonded octachlorodirhenium anions to **1** by simply reacting $[Re_2Cl_8]^{2-}$ with PMe_3 in benzene at room temperature. Complex **1** has an effective magnetic moment of 4.85 μ_B per Re_2 unit, which is consistent with the presence of ca. 4 unpaired electrons per dirhenium unit. As expected, the paramagnetic compound **1** displayed a poorly defined ESR spectrum in frozen CH_2Cl_2 at 77 K. CV data showed several accessible oxidation and reduction processes, but all of them were irreversible. Although the total yield of pure crystalline product **1** is not very high (ca. 35%), complex **1** seems to be an interesting synthetic precursor for further redox reactions. Therefore, in this work we have focused on the reaction chemistry of **1** and accomplished several chemical transformations using complex **1** as a starting material (Scheme 1).

First, one-electron reduction of **1** affords a face-sharing complex of the Re_2^{5+} core, $Re_2(\mu\text{-}Cl)_3Cl_2(PMe_3)_4$ (**2**), in high yield according to reaction 1. This type of structure is rare, and

$$Re_2Cl_6(PMe_3)_4 + KC_8 \rightarrow Re_2(\mu\text{-}Cl)_3Cl_2(PMe_3)_4 + KCl + 8C \quad (1)$$

the only known structural analogue of **2**, the diruthenium compound $Ru_2(\mu\text{-}Cl)_3Cl_2(PMe_3)_4$, was prepared unintentionally as a side product in the synthesis of the $Ru_3Cl_8(PR_3)_4$ by reacting $RuCl_3 \cdot 3H_2O$ with PMe_3 in ethanol.[10] It is worth mentioning that complex **2** has never been seen before in reactions of the $[Re_2Cl_8]^{2-}$ anion in the presence of PMe_3.[1,2]

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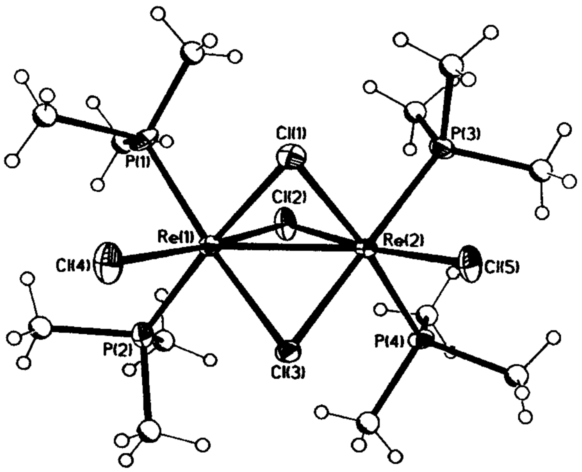

Figure 1. A perspective drawing of the $\mathrm{Re_2(\mu\text{-}Cl)_3Cl_2(PMe_3)_4}$ (**2**) molecule. Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and hydrogen atoms are shown as spheres of arbitrary radii.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $\mathrm{Re_2(\mu\text{-}Cl)_3Cl_2(PMe_3)_4}$ (**2**)

Re(1)−Re(2)	2.686(1)		
Re(1)−P(1)	2.376(6)	Re(2)−P(3)	2.389(6)
Re(1)−P(2)	2.349(6)	Re(2)−P(4)	2.349(6)
Re(1)−Cl(1)	2.496(5)	Re(2)−Cl(1)	2.492(5)
Re(1)−Cl(2)	2.421(5)	Re(2)−Cl(2)	2.423(5)
Re(1)−Cl(3)	2.468(5)	Re(2)−Cl(3)	2.476(5)
Re(1)−Cl(4)	2.394(5)	Re(2)−Cl(5)	2.371(5)
P(1)−Re(1)−P(2)	97.1(2)	P(3)−Re(2)−P(4)	95.7(2)
P(1)−Re(1)−Cl(1)	89.7(2)	P(3)−Re(2)−Cl(1)	91.6(2)
P(1)−Re(1)−Cl(2)	81.9(2)	P(3)−Re(2)−Cl(2)	86.9(2)
P(1)−Re(1)−Cl(3)	171.0(2)	P(3)−Re(2)−Cl(3)	169.8(2)
P(1)−Re(1)−Cl(4)	91.5(2)	P(3)−Re(2)−Cl(5)	85.4(2)
P(2)−Re(1)−Cl(1)	172.5(2)	P(4)−Re(2)−Cl(1)	172.7(2)
P(2)−Re(1)−Cl(2)	89.9(2)	P(4)−Re(2)−Cl(2)	86.9(2)
P(2)−Re(1)−Cl(3)	91.2(2)	P(4)−Re(2)−Cl(3)	90.9(2)
P(2)−Re(1)−Cl(4)	87.1(2)	P(4)−Re(2)−Cl(5)	91.8(2)
Cl(1)−Re(1)−Cl(2)	94.3(2)	Cl(1)−Re(2)−Cl(2)	94.3(2)
Cl(1)−Re(1)−Cl(3)	81.9(2)	Cl(1)−Re(2)−Cl(3)	81.8(2)
Cl(1)−Re(1)−Cl(4)	89.5(2)	Cl(1)−Re(2)−Cl(5)	88.0(2)
Cl(2)−Re(1)−Cl(3)	101.5(2)	Cl(2)−Re(2)−Cl(3)	101.2(2)
Cl(2)−Re(1)−Cl(4)	172.4(2)	Cl(2)−Re(2)−Cl(5)	172.0(2)
Cl(3)−Re(1)−Cl(4)	85.5(2)	Cl(3)−Re(2)−Cl(5)	86.6(2)

Second, two-electron reduction of **1** gives a complex of the $\mathrm{Re_2^{4+}}$ core, namely, 1,2,7,8-$\mathrm{Re_2Cl_4(PMe_3)_4}$ (**3**), which we have isolated before[2], but using a different approach:

$$\mathrm{Re_2Cl_6(PMe_3)_4 + 2KC_8 \rightarrow Re_2Cl_4(PMe_3)_4 + 2KCl + 16C} \tag{2}$$

The preparation, crystal structure, and full characterization of **3** have been presented in detail earlier,[2] and all characteristics of **3** obtained here were identical with those previously reported. Complex **3** was synthesized earlier[2] by one-electron reduction of 1,2,7-$\mathrm{Re_2Cl_5(PMe_3)_3}$ followed by a nonredox substitution of the chloride in the resulting anionic species with $\mathrm{PMe_3}$. The lack of a quantitative method to produce the previous starting material (1,2,7-$\mathrm{Re_2Cl_5(PMe_3)_3}$ tends to cocrystallize[11a] with one molecule of tetrabutylammonium chloride) is a great impediment to the use of that reaction. Therefore, the new route to this triply bonded complex **3** which we are reporting here is of importance. Interestingly, reaction 2 is a stereochemically clean one; only the 1,2,7,8 isomer of $\mathrm{Re_2Cl_4(PMe_3)_4}$ is formed. A cis arrangement of trimethylphosphine ligands in the starting material has been retained upon two-electron reduction in the product **3**.

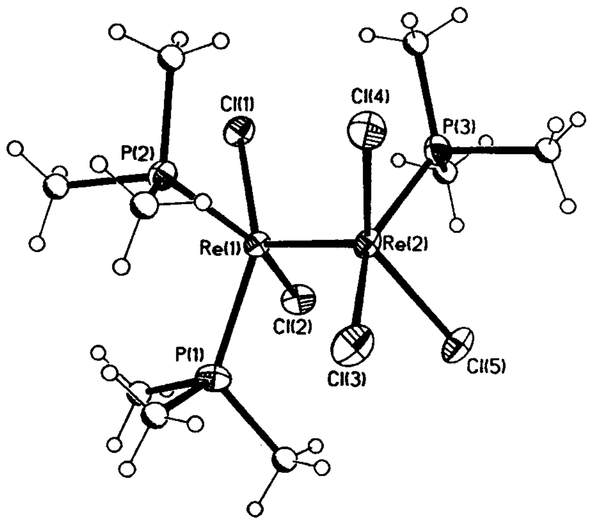

Figure 2. A perspective drawing of the anion $\mathrm{[1,2,7\text{-}Re_2Cl_5(PMe_3)_3]^-}$ in **4**. Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and hydrogen atoms are shown as spheres of arbitrary radii.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $\mathrm{[Bu_4{}^nN][1,2,7\text{-}Re_2Cl_5(PMe_3)_3]}$ (**4**)

Re(1)−Re(2)	2.2354(7)		
Re(1)−P(1)	2.353(3)	Re(2)−P(3)	2.358(3)
Re(1)−P(2)	2.356(3)	Re(2)−Cl(3)	2.425(3)
Re(1)−Cl(1)	2.418(3)	Re(2)−Cl(4)	2.382(3)
Re(1)−Cl(2)	2.449(3)	Re(2)−Cl(5)	2.373(3)
P(1)−Re(1)−P(2)	96.9(1)	P(3)−Re(2)−Cl(4)	86.2(1)
P(1)−Re(1)−Cl(1)	145.6(1)	P(3)−Re(2)−Cl(3)	153.6(1)
P(1)−Re(1)−Cl(2)	82.7(1)	P(3)−Re(2)−Cl(5)	87.2(1)
P(2)−Re(1)−Cl(1)	84.6(1)	Cl(3)−Re(2)−Cl(4)	84.1(1)
P(2)−Re(1)−Cl(2)	156.4(1)	Cl(4)−Re(2)−Cl(5)	138.5(1)
Cl(1)−Re(1)−Cl(2)	82.8(1)	Cl(3)−Re(2)−Cl(5)	84.1(1)
Re(2)−Re(1)−P(1)	97.47(8)	Re(1)−Re(2)−P(3)	94.84(8)
Re(2)−Re(1)−P(2)	95.17(8)	Re(1)−Re(2)−Cl(3)	111.55(9)
Re(2)−Re(1)−Cl(1)	116.73(7)	Re(1)−Re(2)−Cl(4)	114.25(8)
Re(2)−Re(1)−Cl(2)	108.32(8)	Re(1)−Re(2)−Cl(5)	107.12(8)

A new complex of the $\mathrm{Re_2^{4+}}$ core, $\mathrm{[Bu^n{}_4N][Re_2Cl_5(PMe_3)_3]}$ (**4**), was synthesized when the starting material **1** was reduced by 2 equiv of $\mathrm{KC_8}$ in the presence of tetrabutylammonium chloride according to reaction 3.

$$\mathrm{Re_2Cl_6(PMe_3)_4 + [Bu^n{}_4N]Cl + 2KC_8 \rightarrow [Bu^n{}_4N][Re_2Cl_5(PMe_3)_3] + 2KCl + 16C + PMe_3} \tag{3}$$

Complex **4** is a new example of the [1,2,7-$\mathrm{M_2X_5L_3}$] type structure; it is the second one for the $\mathrm{Re_2^{4+}}$ core. Such a 1,2,7-isomer was previously reported for the $\mathrm{Re_2^{5+}}$ core in 1,2,7-$\mathrm{Re_2Cl_5(PMe_3)_3}$.[11] We have earlier reported[12] the synthesis of the analogous anion with $\mathrm{PMe_2Ph}$ ligands, which was accomplished by one-electron reduction of 1,2,7-$\mathrm{Re_2Cl_5(PMe_2Ph)_3}$ with $\mathrm{KC_8}$ followed by cation exchange with $\mathrm{[Bu^n{}_4N]Cl}$ during crystallization. We have confirmed that **4** can be also obtained by

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[11] (a) Cotton, F. A.; Dikarev, E. V. *Inorg. Chem.* **1996**, *35*, 4738. (b) Cotton, F. A.; Price, A. C.; Vidyasagar, K. *Inorg. Chem.* **1990**, *29*, 5143.

[12] Angaridis P. A., Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A., *Inorg. Chim. Acta*, submitted.

Table 4. Key Molecular Dimensions (Å and deg) for 1,2,7-$Re_2Cl_5(PMe_3)_3$, 1,2,7,8-$Re_2Cl_4(PMe_3)_4$, and 1,2,7-$[Re_2Cl_5(PMe_3)_3]^-$ in **4**

	Re_2^{5+}	Re_2^{4+}	
core formula ref	1,2,7-$Re_2Cl_5(PMe_3)_3$[a]	1,2,7,8-$Re_2Cl_4(PMe_3)_4$[b]	[1,2,7-$Re_2Cl_5(PMe_3)_3]^-$ [c]
Re−Re	2.226(1)	2.2414(8)	2.2354(7)
Re−P	2.410(2)	2.373(7)	2.357(4)
Re−Cl	2.360(2)	2.410(8)	2.409(3)
P−Re−P	96.60(7)	92.3(2)	96.9(1)
P(1)−Re−Re−Cl(3)	20.0	2.4	27.9
P(2)−Re−Re−Cl(4)	16.6		23.1
Cl(1)−Re−Re−P(3)	16.4		24.4
Cl(2)−Re−Re−Cl(5)	11.0		22.2

[a] Reference 11. [b] Reference 2. [c] This work.

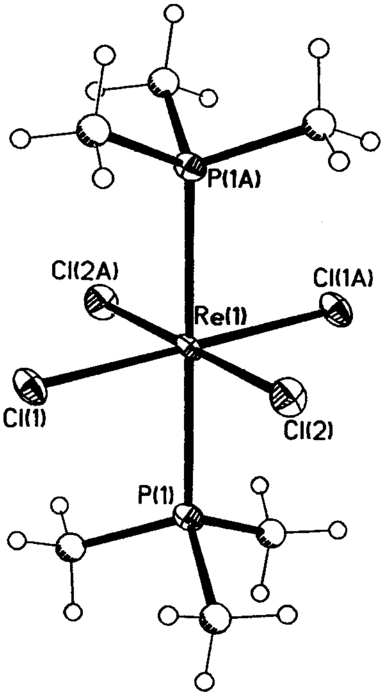

Figure 3. A perspective drawing of the *trans*-$ReCl_4(PMe_3)_2$ (**5**) molecule. Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and hydrogen atoms are shown as spheres of arbitrary radii.

this second procedure (eq 4). It worth mentioning here that the

$$1,2,7\text{-}Re_2Cl_5(PMe_3)_3\cdot[Bu^n{}_4N]Cl + KC_8 \rightarrow [Bu^n{}_4N][Re_2Cl_5(PMe_3)_3] + KCl + 8C \quad (4)$$

1,3,6-isomers of the $[Re_2Cl_5(PR_3)_3]^-$ anions were obtained[13] from the cobaltocene reduction of $Re_2Cl_5(PR_3)_3$; their electrochemical properties have been reported.[13]

Our synthetic route from the non-M−M-bonded system in **1** to the triple bonds in **3** and **4** is of special interest in several respects: (i) both reactions 2 and 3 are completed within several minutes at room temperature; (ii) they give exclusively the desired products with the Re_2^{4+} core in high yields; (iii) the products are stereochemically pure, being only of the cis type.

When we tried to reduce **1** by cobaltocene, complex **2** was obtained as the main product, although not in good yield, but it was contaminated with the mononuclear Re^{III} compound, $[Co(\eta^5\text{-}C_5H_5)_2][cis\text{-}ReCl_4(PMe_3)_2]$ (**7**).

$$3Re_2Cl_6(PMe_3)_4 + 2Co(C_5H_5)_2 \rightarrow 2Re_2Cl_5(PMe_3)_4 + 2[Co(C_5H_5)_2][ReCl_4(PMe_3)_2] \quad (5)$$

Table 5. Selected Bond Distances (Å) and Angles (deg) for *trans*-$ReCl_4(PMe_3)_2$ (**5**)

Re(1)−P(1)	2.491(3)	Re(1)−Cl(2)	2.326(3)
Re(1)−Cl(1)	2.349(2)		
P(1)−Re(1)−Cl(1)	87.4(1)	P(1)−Re(1)−Cl(2)	91.59(9)
P(1)−Re(1)−Cl(1A)	92.6(1)	P(1)−Re(1)−Cl(2A)	88.41(9)
Cl(1)−Re(1)−Cl(2)	89.60(9)	Cl(1)−Re(1)−Cl(2A)	90.40(9)

Therefore, this synthetic route is not as efficient as the use of KC_8 for the preparation of the dirhenium(II) species, at least, in our hands. Nevertheless, the reaction we accomplished results in an interesting monomeric rhenium(III) product. Although the scission of the dirhenium unit has occurred in the course of the reaction, the cis disposition of the trimethylphosphine ligands in **7** has been retained (vide infra). A more efficient and higher yield route to synthesize this product could probably be based on the direct reaction:

$$[cis\text{-}ReCl_4(THF)_2] + Co(C_5H_5)_2 + 2\,PMe_3 \rightarrow [Co(\eta^5\text{-}C_5H_5)_2][cis\text{-}ReCl_4(PMe_3)_2] + 2THF \quad (6)$$

Oxidation of **1** with 1 equiv of $NOBF_4$ results in the cleavage of the dirhenium unit and affords the mononuclear rhenium species *trans*-$ReCl_4(PMe_3)_2$ (**5**) as the main product. This oxidation reaction was not stoichiometric, and there were visible side products. One of them, we suspect, could be the known dirhenium dication $[Re_2Cl_4(PMe_3)_4]^{2+}$.

$$2Re_2Cl_6(PMe_3)_4 + 2NOBF_4 \rightarrow 2ReCl_4(PMe_3)_2 + [Re_2Cl_4(PMe_3)_4](BF_4)_2 + 2NO \quad (7)$$

When **1** was contaminated with tetrabutylammonium chloride, the second side product was identified by X-ray crystallography to be the rhenium(II) mononuclear complex $[Bu^n{}_4N][trans\text{-}ReCl_4(PMe_3)_2]$ (**6**).

$$Re_2Cl_6(PMe_3)_4 + NOBF_4 + 2[Bu^n{}_4N]Cl \rightarrow ReCl_4(PMe_3)_2 + [Bu^n{}_4N][ReCl_4(PMe_3)_2] + [Bu^n{}_4N](BF_4) + NO \quad (8)$$

Structural Descriptions. $Re_2(\mu\text{-}Cl)_3Cl_2(PMe_3)_4$ (2) crystallizes in the monoclinic space group $P2_1$ with two molecules per unit cell. It is isostructural with the analogous diruthenium complex, $Ru_2Cl_5(PMe_3)_4$.[10] Complex **2** (Figure 1) is the first face-sharing bioctahedral complex of this stoichiometry for rhenium. There is no crystallographic symmetry for this molecule, in which two independent rhenium atoms (in formal oxidation states II and III) are bridged by three chloride ligands. However, the $Re_2Cl_5P_4$ core has idealized C_{2v} symmetry and

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

Table 6. Structural Data for *trans*-$ReCl_4P_2$ Cores

complex	Re−Cl	Re−P	ref
$ReCl_4(PMe_3)_2$	2.326(3) 2.349(2)	2.491(3)	this work
$ReCl_4(PEt_3)_2$	2.334(2) 2.339(2)	2.518(1)	16
	2.335(1) 2.337(1)	2.518(1)	15
$ReCl_4(PPr_3)_2$	2.334(1) 2.343(1)	2.513(1)	15
$ReCl_4(PPh_3)_2$	2.3203(8) 2.3300(8)	2.5696(8)	17
	2.326(2) 2.331(2)	2.567(2)	17
$ReCl_4(P(C_7H_7)_3)_2$	2.321(2) 2.339(2)	2.556(2)	18

Table 7. Selected Bond Distances (Å) and Angles (deg) for $[Bu^n_4N][$*trans*-$ReCl_4(PMe_3)_2]$ (**6**) and $[Co(\eta^5\text{-}C_5H_5)_2][$*cis*-$ReCl_4(PMe_3)_2]$ (**7**)

	6	**7**
Re(1)−P(1)	2.414(2)	2.382(2)
Re(1)−P(2)	2.420(2)	2.380(2)
Re(1)−Cl(1)	2.389(2)	2.461(2)
Re(1)−Cl(2)	2.400(2)	2.374(2)
Re(1)−Cl(3)	2.393(2)	2.477(2)
Re(1)−Cl(4)	2.385(2)	2.365(2)
P(1)−Re(1)−P(2)	178.31(7)	95.72(7)
P(1)−Re(1)−Cl(1)	88.43(8)	172.55(7)
P(1)−Re(1)−Cl(2)	89.76(7)	94.36(8)
P(1)−Re(1)−Cl(3)	91.5(1)	88.11(7)
P(1)−Re(1)−Cl(4)	89.57(7)	84.42(7)
P(2)−Re(1)−Cl(1)	92.70(7)	89.83(7)
P(2)−Re(1)−Cl(2)	91.53(7)	84.48(7)
P(2)−Re(1)−Cl(3)	87.46(9)	172.30(7)
P(2)−Re(1)−Cl(4)	89.16(8)	93.14(7)
Cl(1)−Re(1)−Cl(2)	88.24(8)	91.12(7)
Cl(1)−Re(1)−Cl(3)	178.34(9)	86.98(7)
Cl(1)−Re(1)−Cl(4)	90.62(9)	90.32(6)
Cl(2)−Re(1)−Cl(3)	90.1(1)	88.58(7)
Cl(2)−Re(1)−Cl(4)	178.70(9)	177.21(7)
Cl(3)−Re(1)−Cl(4)	91.0(1)	93.88(7)

the Re atoms are chemically equivalent. Average $Re-Cl_{br}$ distances are 2.483(5) Å (trans to P) and 2.422(5) Å (trans to Cl), and the $Re-Cl_{br}-Re$ angles average to 66.1(1)° (Table 2). The Re−Re distance of 2.686(1) Å is much shorter than the Ru−Ru distance (2.992(1) Å) in the diruthenium analogue.[10] Each rhenium atom has one terminal chloride ($Re-Cl_t$ = 2.382(5) Å) and two trimethylphosphine ligands cis to each other (Re−P = 2.366(6) Å; the P−Re−P angle is 96.4(2)°). The average of the bridging Re−Cl bonds is longer than the average of the terminal Re−Cl bonds by more than 0.07 Å. The two rhenium octahedra are very similar to one another.

$[Bu^n_4N][1,2,7\text{-}Re_2Cl_5(PMe_3)_3]$ (4) crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. It consists of the $[Bu^n_4N]^+$ cations and the $[Re_2Cl_5(PMe_3)_3]^-$ anions depicted in Figure 2. Selected bond lengths and angles are given in Table 3.

The metal−metal distance of 2.2354(7) Å in the dirhenium anion is typical for the Re_2^{4+} core triply bonded compounds (cf. 2.2414(8) Å in 1,2,7,8-$Re_2Cl_4(PMe_3)_4$).[2] An interesting feature of **4** is the fact that phosphine ligands on one rhenium atom are located cis to each other with a P−Re−P angle of 96.9(1)° and an average Re−P distance of 2.357(4) Å, which is very close to the one in 1,2,7-$Re_2Cl_5(PMe_3)_3$.[11] Table 4 shows that key molecular characteristics of the dirhenium anion in **4** are intermediate between those in 1,2,7-$Re_2Cl_5(PMe_3)_3$ and 1,2,7,8-$Re_2Cl_4(PMe_3)_4$. Interestingly, the torsion angles in the anion in **4** are even larger than those in the neutral 1,2,7-$Re_2Cl_5(PMe_3)_3$ molecule.

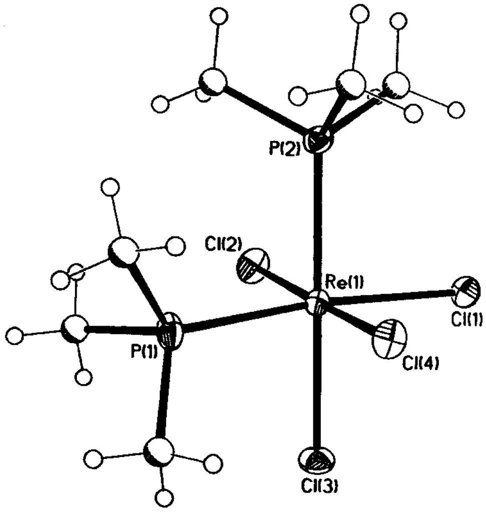

Figure 4. A perspective drawing of the $[$*cis*-$ReCl_4(PMe_3)_2]^-$ anion in **7**. Atoms are represented by thermal ellipsoids at the 40% probability level. Carbon and hydrogen atoms are shown as spheres of arbitrary radii.

The dirhenium anion in **4** is only the second example of the Re_2^{4+} core in this structure (we have synthesized its dimethylphenylphosphine analogue recently[12]), thus expanding the class of all known dirhenium complexes in which there is a cis arrangement of monodentate phosphines.[1,11−14]

***trans*-$ReCl_4(PMe_3)_2$ (5)** crystallizes in the monoclinic $P2_1/c$ space group with the molecule residing on a center of inversion (Figure 3). The central $ReCl_4P_2$ group has essentially D_{4h} symmetry, as can be seen from the distances and angles listed in Table 5. Thus, all trans angles are equal to 180° by symmetry, and cis angles are all close to 90°.

trans-$ReCl_4(PMe_3)_2$ has a structure very similar to those of previously reported analogues, namely, $ReCl_4(PEt_3)_2$,[15,16] $ReCl_4(PPr^n_3)_2$,[15] $ReCl_4(PPh_3)_2$,[17] and $ReCl_4(P(C_7H_7)_3)_2$,[18] with mean Re−Cl distances being essentially the same in all Re^{IV} compounds. The trend of increasing the Re−P bond length with the growth of steric hindrance from the bulky phosphines can be seen from Table 6. The Re−P distance of 2.491(3) Å in **5** is the shortest among compounds of this type.

$[Bu^n_4N][$*trans*-$ReCl_4(PMe_3)_2]$ (6) crystallizes in the monoclinic $P2_1/c$ space group with four molecules per unit cell. It is composed of the rhenium(III) anions $[ReCl_4(PMe_3)_2]^-$ and tetrabutylammonium cations. Selected bond distances and angles for **6** are listed in Table 7. In the distorted octahedral core, $ReCl_4P_2$, two phosphine ligands are located trans to each other with the Re−P distances averaged to 2.417(2) Å and the P−Re−P angle of 178.31(7)°. The $Re^{3+}-Cl$ distances are all very close and averaged to 2.392(2) Å, about 0.05 Å longer than $Re^{4+}-Cl$ bonds in **5**.

$[Co(\eta^5\text{-}C_5H_5)_2][$*cis*-$ReCl_4(PMe_3)_2]$ (7) crystallizes in the monoclinic $P2_1/c$ space group with four molecules per unit cell.

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It consists of rhenium anions $[ReCl_4(PMe_3)_2]^-$ and cobaltocenium cations. Selected bond distances and angles for **7** are presented in Table 7 along with corresponding data for **6**.

The rhenium atom in the [*cis*-$ReCl_4(PMe_3)_2]^-$ anion exhibits a distorted octahedral geometry (Figure 4) for the $ReCl_4P_2$ core. Two trimethylphosphine ligands are coordinated cis to each other with an average Re−P distance of 2.381(2) Å and a P−Re−P angle of 95.72(7)°. The average Re−Cl (trans to P) distances are 2.469(2) Å, while Re−Cl (trans to Cl) are significantly shorter (2.370(2) Å). The $[\eta^5\text{-}Co(C_5H_5)_2]^+$ cations are well separated from the anions in the crystalline lattice and have an average Co−C distance of 2.018(9) Å.

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

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