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Mixed Chloride/Phosphine Complexes of the Dirhenium Core. 8. Synthesis and Crystal Structure of the Quadruply Bonded Dirhenium(III) Anion $[Re_2Cl_7(PMe_3)]^-$

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Introduction

The dirhenium(III) anionic complexes of the type $[Re_2Cl_7(PR_3)]^-$ are the least studied among the entire class of $Re_2Cl_{8-x}(PR_3)_x$ ($x = 1, 2, 3,$ and 4) molecules. They have been characterized by McArdle and co-workers only for a few bulky and not very basic monodentate phosphines, $PR_3 = PBu^n{}_3$ and PBu^nPh_2,[1] $PBu^n{}_2Ph$, [2] and PBzPhMe.[3] They were isolated as intermediates in the conversion of $[Re_2Cl_8]^{2-}$ to $Re_2Cl_6(PR_3)_2$ by the stepwise replacement of two chlorides by phosphines. Attempts to extend the range of ligands to other tertiary phosphines met with little success.[4] For the most basic PMe_3 ligand, it was impossible to stop the reaction at the first substitution step, as it easily proceeds further to form the $Re_2{}^{5+}$ and $Re_2{}^{4+}$ core complexes.[5,6] Therefore, in the present work we offer an alternate synthetic route toward the preparation of the $[Re_2Cl_7(PR_3)]^-$ anions, which is based on the one-electron oxidation of the $Re_2Cl_5(PR_3)_3$ in the presence of 2 equiv of a chloride source. We have tried it here for the most basic monodentate phosphine, PMe_3, and a readily available starting material, namely, 1,2,7-$Re_2Cl_5(PMe_3)_3 \cdot [Bu^n{}_4N]Cl$ (**1**).[5] It is worth mentioning that we have already shown that the one-electron oxidation reaction of **1** affords the dirhenium(III) complex $Re_2Cl_6(PMe_3)_2$ (**2**) in good yield.[6] By adding an extra equivalent of the $[Bu^n{}_4N]Cl$ to the reaction mixture, we have now prepared the desired anionic complex $[Re_2Cl_7(PMe_3)]^-$. It has been isolated in the form of $[Bu^n{}_4N]_4[Re_2Cl_7(PMe_3)]_2[Re_2Cl_8] \cdot 2CH_2Cl_2$ (**3**), which has been crystallographically and spectroscopically characterized.

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: $[Bu^n{}_4N]_2[Re_2Cl_8]$, $[Bu^n{}_4N]Cl$, and $NOBF_4$ (Aldrich, Inc.); PMe_3 (Strem Chemicals); chloroform-d_1 and dichloromethane-d_2 (Cambridge Isotope Laboratories). 1,2,7-$Re_2Cl_5(PMe_3)_3 \cdot [Bu^n{}_4N]Cl$ (**1**) was prepared according to a literature procedure.[5]

Physical Measurements. The $^{31}P\ \{^1H\}$ NMR data were recorded at room temperature on a UNITY-plus 300 multinuclear spectrometer operated at 121.4 MHz using 85% H_3PO_4 as an external standard. Electrochemical measurements were carried out under an N_2 atmosphere on dichloromethane solutions that contained 0.1 M $[Bu^n{}_4N]PF_6$ as the supporting electrolyte. $E_{1/2}$ 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., model 100 electrochemical analyzer. The scan rate was 100 mV/s at a Pt disk electrode.

Synthesis of $[Bu^n{}_4N]_4[Re_2Cl_7(PMe_3)]_2[Re_2Cl_8] \cdot 2CH_2Cl_2$ (3). 1,2,7-$Re_2Cl_5(PMe_3)_3 \cdot [Bu^n{}_4N]Cl$ (0.109 g, 0.10 mmol) was dissolved in 10 mL of CH_2Cl_2, and the dichloromethane solution was added by cannula to the Schlenk flask containing a mixture of the following solids: $NOBF_4$ (0.013 g, 0.11 mmol) and $[Bu^n{}_4N]Cl$ (0.027 g, 0.10 mmol). The resulting mixture was stirred for 1 h at room temperature to give a dirty-green solution. The solvent was removed from the solution to leave a green-brown solid. The solid was washed with hexanes, dried, and then dissolved in 10 mL of CH_2Cl_2, and the dichloromethane solution was layered with 15 mL of hexanes. Blue-green plate-shaped crystals of **3** appeared in a few days. Yield: 0.081 g (81%). ^{31}P NMR ($CDCl_3$, 20 °C): δ −20.3 (s). CV (CH_2Cl_2, 22 °C, V vs Ag/AgCl): for $[Re_2Cl_7(PMe_3)]^-$, $E_{1/2}(\text{red}) = -0.39$; for $[Re_2Cl_8]^{2-}$, $E_{1/2}(\text{ox}) = +1.21$, $E_{1/2}(\text{red}) = -0.87$.

Along with **3**, a few green blocks of $Re_2Cl_6(PMe_3)_2$ (**2**) have been found; as these crystals have distinctly different shapes and colors, they were separated manually. **2**. ^{31}P NMR (CD_2Cl_2, 20 °C): δ 3.05 (s). CV (CH_2Cl_2, 22 °C, V vs Ag/AgCl): $E_{1/2}(\text{red})$ (**1**) $= +0.02$, $E_{1/2}(\text{red})$ (**2**) $= -1.04$.

X-ray Crystallographic Procedures. Single crystals of compounds **2** and **3** were obtained as described above. The X-ray diffraction studies were carried out on a Nonius FAST diffractometer with an area detector using Mo Kα radiation. Details of data collection have been fully described elsewhere.[7] Each crystal was mounted on the tip of a quartz fiber with silicone grease, and the setup was quickly placed in the cold N_2 stream (−60 °C) of a model FR 558-S low-temperature controller. Fifty reflections were used in cell indexing, and 250 reflections in cell refinement. Axial images were used to confirm the Laue group and all dimensions. The data were corrected for Lorentz and polarization effects by the MADNES program.[8] Reflection profiles were fitted, and values of F^2 and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR.[9] All calculations were carried out on a DEC Alpha running VMS. The structures were solved and refined using the SHELXTL direct methods[10] and SHELXL-93 programs.[11] All hydrogen atoms for **2** and **3** were included in the structure factor calculations at idealized positions. Relevant crystallographic data for both complexes are summarized in Table 1.

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Table 1. Crystallographic Data for $Re_2Cl_6(PMe_3)_2$ (**2**) and $[Bu^n{}_4N]_4[Re_2Cl_7(PMe_3)]_2[Re_2Cl_8]\cdot 2CH_2Cl_2$ (**3**)

	2	**3**
chemical formula	$Re_2P_2Cl_6C_6H_{18}$	$Re_6P_2N_4Cl_{26}C_{72}H_{166}$
formula weight	737.24	3188.93
space group (No.)	$P2_1/c$ (No. 14)	*Pbca* (No. 61)
a, Å	11.625(6)	15.813(4)
b, Å	12.387(4)	17.804(5)
c, Å	12.779(3)	40.935(6)
β, deg	92.09(3)	
V, Å^3	1839(1)	11525(5)
Z	4	4
D_{calcd}, g/cm^3	2.663	1.838
μ, mm^{-1}	14.175	6.944
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
T, °C	−60	−60
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0498, 0.1081	0.0678, 0.1459
R1,[a] wR2[b] (all data)	0.0560, 0.1121	0.0925, 0.1597

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

Results and Discussion

Prior to this work, a quantitative method to isolate the $Re^{II,III}$ complex 1,2,7-$Re_2Cl_5(PMe_3)_3$, cocrystallized with $[Bu^n{}_4N]Cl$ in a 1:1 ratio by reaction of $[Re_2Cl_8]^{2-}$ with PMe_3 in 1-propanol at room temperature, was reported.[5] The ready availability of this complex, 1,2,7-$Re_2Cl_5(PMe_3)_3$, enabled its use as a starting material in syntheses of molecules with a *cis* geometry of phosphines on the rhenium atoms, especially in redox reactions, as it is known to exhibit very accessible redox potentials.[6]

We have previously reported[6] that the one-electron oxidation of 1,2,7-$Re_2Cl_5(PMe_3)_3$, accomplished in the presence of precisely 1 equiv of tetrabutylammonium chloride, results in the dirhenium(III) complex 1,7-$Re_2Cl_6(PMe_3)_2$ according to the following reaction:

$$Re_2Cl_5(PMe_3)_3\cdot[Bu^n{}_4N]Cl + NOBF_4 \rightarrow Re_2Cl_6(PMe_3)_2 + NO + [Bu^n{}_4N]BF_4 + PMe_3 \quad (1)$$

Here we attempted the monoelectronic oxidation of the 1,2,7-$Re_2Cl_5(PMe_3)_3\cdot[Bu^n{}_4N]Cl$ complex by $NOBF_4$ in the presence of an additional 1 equiv of tetrabutylammonium chloride in order to get the dirhenium(III) complex of the $[Bu^n{}_4N][Re_2Cl_7(PMe_3)]$ stoichiometry, for which no preparation has heretofore been known.[1−4] This reaction was expected to proceed according to the following equation:

$$Re_2Cl_5(PMe_3)_3\cdot[Bu^n{}_4N]Cl + NOBF_4 + [Bu^n{}_4N]Cl \rightarrow [Bu^n{}_4N][Re_2Cl_7(PMe_3)] + NO + [Bu^n{}_4N]BF_4 + 2PMe_3 \quad (2)$$

From the latter reaction, we isolated crystals of the complex $[Bu^n{}_4N]_4[Re_2Cl_7(PMe_3)]_2[Re_2Cl_8]\cdot 2CH_2Cl_2$ (**3**), in which the desired anion $[Re_2Cl_7(PMe_3)]^-$ was cocrystallized with the fully substituted dirhenium(III) octachloride anion, $[Re_2Cl_8]^{2-}$, in a ratio of 2:1. CV data for **3** were consistent with the presence of both dirhenium anions in dichloromethane solution, and the value of the first redox potential for the title anion, $[Re_2Cl_7(PMe_3)]^-$, was in agreement with that reported for the $[Re_2Cl_7(PBu^nPh_2)]^-$.[1] In addition, a few crystals of $Re_2Cl_6(PMe_3)_2$ (**2**) have been found mixed with those of **3**. This can be explained by the fact that the substitution reaction of the last phosphine group in the $[Re_2Cl_7(PMe_3)]^-$ by a chloride ion proceeds easily. Thus, as soon as it begins to form, some of it starts to convert further to $[Re_2Cl_8]^{2-}$ anions in the presence of chloride. This leaves some of complex **2** unreacted, and the formation of the observed crystalline products could be described by eq 3:

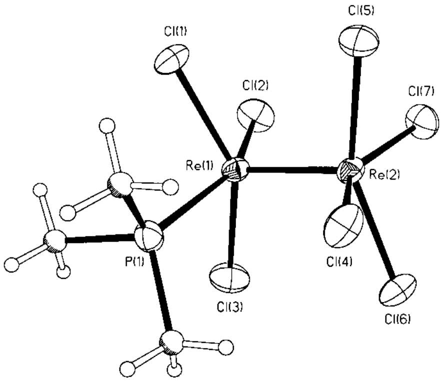

Figure 1. Drawing of the $[Re_2Cl_7(PMe_3)]^-$ anion showing the major Re−Re orientation only. Atoms are represented by thermal ellipsoids at the 30% probability level. Carbon and hydrogen atoms are shown as spheres of an arbitrary radius.

$$Re_2Cl_5(PMe_3)_3\cdot[Bu^n{}_4N]Cl + NOBF_4 + [Bu^n{}_4N]Cl \rightarrow 1/4[Bu^n{}_4N]_4[Re_2Cl_7(PMe_3)]_2[Re_2Cl_8] + 1/4Re_2Cl_6(PMe_3)_2 + NO + [Bu^n{}_4N]BF_4 + 2PMe_3 \quad (3)$$

This does not, however, necessarily correspond to the equilibrium situation in solution. This would be determined by the equilibrium constant for reaction 4, which we have not investigated:

$$2[Re_2Cl_7(PMe_3)]^- \leftrightarrows Re_2Cl_6(PMe_3)_2 + [Re_2Cl_8]^{2-} \quad (4)$$

For the stoichiometry represented in eq 3 to correspond to the equilibrium position in solution, the equilibrium constant for eq 4 would have to be 1, which would be an unlikely coincidence.

This reaction has allowed us for the first time to isolate a compound containing the title anion, $[Re_2Cl_7(PMe_3)]^-$, and to report its structural characteristics. The crystal structure of the product $[Bu^n{}_4N]_4[Re_2Cl_7(PMe_3)]_2[Re_2Cl_8]\cdot 2CH_2Cl_2$ (**3**) has been determined by X-ray crystallography, and a view of the anion $[Re_2Cl_7(PMe_3)]^-$ is depicted in Figure 1. The Re_2 units in the anion are 3-fold disordered within the approximate cube defined by seven chlorine and one phosphorus atoms. The site occupancy factors refined very well to values of 0.903(2), 0.059(2), and 0.038(2). The Re−Re distance for the major orientation is 2.210(1) Å, consistent with the presence of a quadruple bond between the rhenium atoms. Only bond distances and angles involving the dominant Re_2 unit are given in Table 2. The Re−P distance is 2.456(5) Å, while the Re−Cl distances are averaged to 2.321(5) Å. The Re−Cl(2) distance *trans* to P of 2.319(5) Å does not show any significant *trans* influence. The configuration of the $[Re_2Cl_7(PMe_3)]^-$ anion is almost eclipsed with the P−Re−Re−Cl torsion angle of 5.0(2)°, while the Cl−Re−Re−Cl torsion angles averaged to 4.8(2)°.

The structure of the $Re_2Cl_6(PMe_3)_2$ molecule (**2**) in the form of the cubic polymorph was described in detail earlier.[6] Here, a monoclinic polymorph of **2** has been found as a side product of the above-mentioned reaction. A crystal structure determination for **2** has confirmed the 1,7-disposition of phosphines in the centrosymmetric dirhenium $Re_2Cl_6P_2$ core.[12] There are two

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Table 2. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for $[Re_2Cl_7(PMe_3)]^-$ in **3**

Re(1)−Re(2)	2.210(1)		
Re(1)−P(1)	2.456(5)	Re(2)−Cl(4)	2.343(5)
Re(1)−Cl(1)	2.306(4)	Re(2)−Cl(5)	2.325(4)
Re(1)−Cl(2)	2.319(5)	Re(2)−Cl(6)	2.332(4)
Re(1)−Cl(3)	2.310(5)	Re(2)−Cl(7)	2.312(5)
Cl(1)−Re(1)−Cl(2)	88.3(2)	Cl(4)−Re(2)−Cl(5)	86.3(2)
Cl(1)−Re(1)−Cl(3)	148.0(2)	Cl(4)−Re(2)−Cl(6)	86.2(2)
Cl(2)−Re(1)−Cl(3)	89.5(2)	Cl(4)−Re(2)−Cl(7)	148.6(2)
Cl(1)−Re(1)−P(1)	84.0(2)	Cl(5)−Re(2)−Cl(6)	155.0(2)
Cl(2)−Re(1)−P(1)	153.5(2)	Cl(5)−Re(2)−Cl(7)	86.6(2)
Cl(3)−Re(1)−P(1)	83.9(2)	Cl(6)−Re(2)−Cl(7)	87.5(2)
Re(2)−Re(1)−P(1)	100.2(1)	Re(1)−Re(2)−Cl(4)	109.7(1)
Re(2)−Re(1)−Cl(1)	106.1(1)	Re(1)−Re(2)−Cl(5)	102.2(1)
Re(2)−Re(1)−Cl(2)	106.2(1)	Re(1)−Re(2)−Cl(6)	102.7(1)
Re(2)−Re(1)−Cl(3)	105.1(2)	Re(1)−Re(2)−Cl(7)	101.8(1)
P(1)−Re(1)−Re(2)−Cl(4)	5.0(2)		
Cl(1)−Re(1)−Re(2)−Cl(5)	8.7(2)		
Cl(2)−Re(1)−Re(2)−Cl(7)	4.8(2)		
Cl(3)−Re(1)−Re(2)−Cl(6)	0.9(2)		

Scheme 1

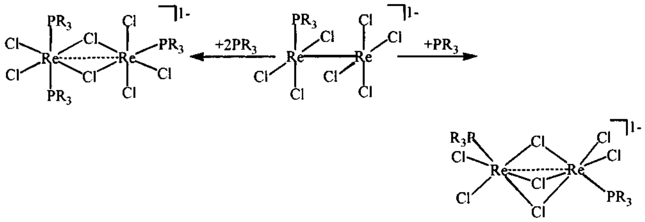
$$[Re_2Cl_8]^{2-} \xleftarrow[-PR_3]{Cl^-} [Re_2Cl_7(PR_3)]^- \xrightarrow[-Cl^-]{PR_3} Re_2Cl_6(PR_3)_2$$

independent dimetal units in the cell, one of which is disordered over two orientations with occupancies of 0.92(1) and 0.08(1). The average Re−Re distance of 2.209(1) Å is consistent with the value of 2.208(1) Å for the cubic polymorph.[6] The rest of the distances and angles also show good agreement between the two polymorphs of $Re_2Cl_6(PMe_3)_2$.

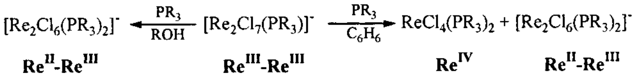
A general preparation for $[Re_2Cl_7(PR_3)]^-$-type compounds is still a synthetic challenge because in the presence of even low concentrations of ligands they readily undergo a substitution in either direction (Scheme 1).

The dirhenium(III) anions $[Re_2Cl_7(PR_3)]^-$ can also add one or two ligands and then convert[13] to face-sharing or edge-sharing complexes (Scheme 2).

Scheme 2



Scheme 3



$$\underset{Re^{II}\text{-}Re^{III}}{[Re_2Cl_6(PR_3)_2]^-} \xleftarrow[ROH]{PR_3} \underset{Re^{III}\text{-}Re^{III}}{[Re_2Cl_7(PR_3)]^-} \xrightarrow[C_6H_6]{PR_3} \underset{Re^{IV}}{ReCl_4(PR_3)_2} + \underset{Re^{II}\text{-}Re^{III}}{[Re_2Cl_6(PR_3)_2]^-}$$

Finally, they can easily undergo reduction to the Re_2^{5+} core species or disproportionation to the Re(IV) and Re(II) compounds[13] in the presence of phosphines (Scheme 3).

Conclusion. Dirhenium(III) complexes of the type $[Re_2Cl_7(PR_3)]^-$ have been isolated so far only as intermediates in the stepwise replacement reactions of two chlorides in the $[Re_2Cl_8]^{2-}$ by monodentate phosphines. These reactions were found to be applicable to a limited number of not very basic tertiary phosphines. For the very basic PR_3 ligands, no generally useful synthetic procedure is yet known. Here, we tested an alternative synthetic route based on the one-electron oxidation of the $Re_2Cl_5(PR_3)_3$ in the presence of a chloride source. In the case of the most basic monodentate phosphine, trimethylphosphine, we have isolated the desired anion $[Re_2Cl_7(PMe_3)]^-$ but only in the form of $[Bu^n{}_4N]_4[Re_2Cl_7(PMe_3)]_2[Re_2Cl_8]$, not as the simple $[Bu^n{}_4N][Re_2Cl_7(PMe_3)]$ compound.

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Supporting Information Available: Two 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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