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Mixed chloride–phosphine complexes of the dirhenium core. Part 11. Reactions of $[Re_2Cl_8]^{2-}$ with secondary phosphines, PCy_2H and PPh_2H

Panagiotis A. Angaridis [a], F. Albert Cotton [a,*], Evgeny V. Dikarev [a,b],
Marina A. Petrukhina [a,b]

[a] *Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A&M University, PO Box 30012, College Station, TX 77842-3012, USA*
[b] *State University of New York at Albany, Department of Chemistry, Albany, NY 12222, USA*

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Abstract

The reaction between the dirhenium(III,III) anion, $[Re_2Cl_8]^{2-}$, and the secondary phosphine, PCy_2H, yields a mixture of products as a result of disproportionation, namely, a dirhenium(II,III) chloride–phosphine complex 1,3,6-$Re_2Cl_5(PCy_2H)_3$ (**1**) and a dirhenium(IV) face-sharing bioctahedral compound with bridging phosphido groups, $[Bu^n_4N][Re_2(\mu\text{-}PCy_2)_3Cl_6]$ (**2**). The diphenylphosphine analogue of **2**, $[Bu^n_4N][Re_2(\mu\text{-}PPh_2)_3Cl_6]$ (**3**) has been similarly prepared from the reaction of $[Re_2Cl_8]^{2-}$ with PPh_2H. An interesting dirhenium(III,III) complex, $[Bu^n_4N]_2[Re_2(\mu\text{-}PPh_2)_2(PPh_2H)_2Cl_6]$ (**4**) having both neutral terminal phosphines and anionic phosphido bridges, has also been isolated as an intermediate in the latter system. Crystal structures of **1**–**4** have been determined by X-ray crystallography. The compounds were also characterized by cyclic voltammetry, IR and ^{31}P NMR spectroscopy. © 2002 Published by Elsevier Science B.V.

Keywords: Phosphine/chloride complexes; Dirhenium(II,III) complexes; X-ray crystallography

1. Introduction

Our previous work on the reactions of the octachlorodirhenium anion, $[Re_2Cl_8]^{2-}$, and monodentate phosphines, revealed that the nature of the solvent has a great influence on the reaction pathway [1,2]. We have shown that a disproportionation process rather than reduction occurs in an inert and nonpolar solvent such as benzene [3]. In the case of tertiary monodentate phosphines, PEt_3 and PPr^n_3, both the reduced and the oxidized rhenium species have been isolated [3]. Some spectroscopic evidence that edge- and face-sharing bioctahedral dirhenium compounds play an important role in those processes at an early stage of the reactions has been presented. Further insight into the disproportionation mechanism as well as identification of the intermediate rhenium species has been of special interest for us since then. Therefore, we extended this study to two monodentate secondary phosphines, namely PCy_2H and PPh_2H. It is known that not only can secondary phosphines react in the same manner as tertiary phosphines, but, also, a deprotonation may occur affording a dialkyl or diaryl phosphido group capable of acting as either a terminal or bridging ligand. This expands the structural possibilities in rhenium chemistry and might stabilize some intermediates in the above-mentioned reactions of $[Re_2Cl_8]^{2-}$ when using secondary phosphine ligands.

As a result of this study, we report here synthetic preparations and the crystal structures of several new dirhenium complexes, namely: a compound of the Re_2^{5+} core, $Re_2Cl_5(PCy_2H)_3$ (**1**), two analogous face-sharing bioctahedral (FSBO) rhenium(IV) complexes, $[Bu^n_4N][Re_2(\mu\text{-}PR_2)_3Cl_6]$ (R = Cy (**2**) and Ph (**3**)), and a novel rhenium(III) edge-sharing bioctahedral (ESBO) compound, $[Bu^n_4N]_2[Re_2(\mu\text{-}PPh_2)_2(PPh_2H)_2Cl_6]$ (**4**).

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* Corresponding author. Tel.: + 1-979-845 4432; fax: + 1-979-845 9351.
E-mail address: cotton@tamu.edu (F.A. Cotton).

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2. Experimental

2.1. General procedures

All 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: PCy_2H and PPh_2H, Strem Chemicals; $[Bu^n_4N]_2[Re_2Cl_8]$, Aldrich, Inc.

2.2. Physical measurements

Electrochemical measurements were carried out on CH_2Cl_2 solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. A stream of dinitrogen 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 (r.t.). Under our experimental conditions, $E_{1/2} = +0.47$ V versus 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^{-1} at a Pt disk electrode. The ^{31}P $\{^1H\}$ NMR data were recorded at r.t. on a UNITY-plus 300 multinuclear spectrometer operated at 121.4 MHz and using 85% H_3PO_4 as an external standard. The IR spectra were performed in the range 400–4000 cm^{-1} on a Perkin–Elmer 16PC FT-IR spectrophotometer using KBr pellets.

2.3. Preparation of $Re_2Cl_5(PCy_2H)_3$ (**1**) and $[Bu^n_4N][Re_2(\mu\text{-}PCy_2)_3Cl_6]$ (**2**)

To a suspension containing $[Bu^n_4N]_2[Re_2Cl_8]$ (0.226 g, 0.2 mmol) in C_6H_6, 0.5 ml of PCy_2H was added at about 0 °C. The mixture was slowly warmed to r.t. and stirred overnight affording a brown solid. It was isolated by filtration, washed with hexanes (2 × 10 ml), dried, and then dissolved in 15 ml of CH_2Cl_2. The CH_2Cl_2 solution was layered with 20 ml of hexanes. Two sorts of crystals appeared in 3 days: brownish block-shaped crystals of **1** and purple plates of **2**, which were separated manually. For **1**: CV (CH_2Cl_2, Ag | AgCl, 22 °C, V): $E_{1/2}$(red) = -0.66, $E_{1/2}$(ox) = $+0.52$. For **2**: ^{31}P NMR $\{CD_2Cl_2$, 22 °C$\}$: δ 221.3 ppm (s).

2.4. Preparation of $[Bu^n_4N][Re_2(\mu\text{-}PPh_2)_3Cl_6]$ (**3**)

To a suspension containing $[Bu^n_4N]_2[Re_2Cl_8]$ (0.222 g, 0.2 mmol) in 15 ml of toluene, 0.6 ml of PPh_2H was added. The mixture was stirred at r.t. for 2 h; it was then refluxed for 2 days affording a very dark brown precipitate. The mixture was cooled and the solid was filtered off. It was washed with hexanes, dried, and then dissolved in 10 ml of CH_2Cl_2 giving a dark purple solution. The CH_2Cl_2 solution was layered with 25 ml of Et_2O. Dark purple, block crystals were grew at the walls of the tube in a few days. They were recrystallized from the acetone–hexanes system affording crystals of **3**. Yield: 40–45%. ^{31}P NMR $\{CD_2Cl_2$, 22 °C$\}$: δ 215.6 ppm (s).

2.5. Preparation of $[Bu^n_4N]_2[Re_2(\mu\text{-}PPh_2)_2(PPh_2H)_2Cl_6]$ (**4**)

To a solution containing $[Bu^n_4N]_2[Re_2Cl_8]$ (0.097 g, 0.085 mmol) in 10 ml of CH_2Cl_2, 0.5 ml of PPh_2H was added. The solution turned brown in a few minutes. It was stirred for 1 h at r.t.. All volatiles were removed under reduced pressure to leave a brown oily solid. It was washed with hexanes (3 × 15 ml), then dissolved in 8 ml of acetone, and the acetone solution was layered with 15 ml of hexanes. Several brown crystals of **4** came out in a week. Yield: approximately 15%. IR (KBr, cm^{-1}): 3051.7(s), 2960.0(s), 2873.1(s), 1617.6(w,br), 1586.9(w), 1572.8(w), 1468.0(s), 1482.8(s), 1435.9(s), 1380.3(s), 1312.7(w), 1333.7(w), 1189.1(w), 1156.9(w), 1129.9(m), 1100.8(s), 1069.9(m), 1028.5(m), 978.0(m), 885.9(s), 805.6(w), 740.09(s), 693.2(s), 535.1(s), 515.7(s), 492.0(s), 423.9(m).

2.6. X-ray structure determinations

Single crystals of compounds **1**$\cdot CH_2Cl_2\cdot 1/2C_6H_{14}$, **2**$\cdot 3/4(CH_3)_2CO$, and **4**$\cdot 31/2(CH_3)_2CO$ were obtained as described above. The X-ray diffraction experiments were carried out on a Nonius FAST diffractometer with an area detector using Mo Kα radiation. The crystals were 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 low temperature controller. Fifty reflections were used in cell indexing and about 250 reflections in cell refinement. The data were corrected for Lorentz and polarization effects by the MADNES program [4]. Reflection profiles were fitted and values of F^2 and $\sigma(F^2)$ for each reflection were obtained by the program PROCOR [5]. The intensities for **2**$\cdot 3/4$ $(CH_3)_2CO$ and **4**$\cdot 31/2$ $(CH_3)_2CO$ were also corrected for absorption using a local adaptation of the program SORTAV [6]. All calculations were done on a DEC Alpha running VMS. The coordinates of rhenium atoms were found in direct *E* maps using the structure solution program SHELXTL [7]. The positions of the remaining atoms were located by means of alternating series of least-squares cycles and difference Fourier maps [8]. Anisotropic displacement parameters were

Table 1
Crystallographic data for 1,3,6-$Re_2Cl_5(PCy_2H)_3 \cdot CH_2Cl_2 \cdot 1/2C_6H_{14}$ (**1**$\cdot CH_2Cl_2 \cdot 1/2C_6H_{14}$), $[Bu^n_4N][Re_2(\mu\text{-}PCy_2)_3Cl_6] \cdot 3/4(CH_3)_2CO$ (**2**$\cdot 3/4(CH_3)_2CO$) and $[Bu^n_4N]_2[Re_2(\mu\text{-}PPh_2)_2Cl_6(PPh_2H)_2] \cdot 31/2(CH_3)_2CO$ (**4**$\cdot 31/2(CH_3)_2CO$)

	1$\cdot CH_2Cl_2 \cdot 1/2C_6H_{14}$	**2**$\cdot 3/4(CH_3)_2CO$	**4**$\cdot 31/2(CH_3)_2CO$
Formula	$C_{40}H_{78}Cl_7P_3Re_2$	$C_{54.25}H_{106.50}Cl_6N_1O_{0.75}P_3Re_2$	$C_{90.50}H_{135}Cl_6N_2O_{3.50}P_4Re_2$
Formula weight	1272.48	1462.91	2015.99
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1$	$P\bar{1}$
a (Å)	10.721(3)	13.670(4)	14.562(4)
b (Å)	20.501(9)	23.350(8)	15.074(4)
c (Å)	24.000(3)	20.357(5)	23.214(4)
α (°)			90.35(2)
β (°)	101.48(2)	90.81(3)	106.91(2)
γ (°)			99.94(2)
V (Å^3)	5170(3)	6497(3)	4794(2)
Z	4	4	2
ρ_{calc} (g cm^{-3})	1.635	1.496	1.397
μ (mm^{-1})	5.160	4.078	2.803
Radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
Temperature (K)	213(2)	213(2)	213(2)
Transmission factors		0.379–0.554	0.329–0.580
Number of unique data	6763	16 185	11 996
Number of observed data [$I > 2\sigma(I)$]	5639	15 447	10 593
Number of parameters refined	455	1185	930
R_1 [a], wR_2 [b] [$I > 2\sigma(I)$]	0.0709, 0.1600	0.0435, 0.1041	0.0477, 0.1165
R_1 [a], wR_2 [b] (all data)	0.0887, 0.1809	0.0475, 0.1090	0.0562, 0.1266
Quality-of-fit [c]	1.136	1.114	1.106

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

[c] Quality-of-fit $= [\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{1/2}$, based on all data.

assigned to all non-hydrogen atoms. Hydrogen atoms were included in the structure factor calculations at idealized positions. The hydrogen atoms connected to the phosphorus atoms of PPh_2H in **4** were found in a difference Fourier map and then refined independently with an isotropic thermal parameter.

Relevant crystallographic data for **1**$\cdot CH_2Cl_2 \cdot 1/2C_6H_{14}$, **2**$\cdot 3/4(CH_3)_2CO$, and **4**$\cdot 31/2(CH_3)_2CO$ are summarized in Table 1, and selected bond distances and angles are given in Tables 2–4.

3. Results

The molecular structures of the four compounds are shown schematically in Chart 1.

3.1. $Re_2Cl_5(PCy_2H)_3 \cdot CH_2Cl_2 \cdot 1/2C_6H_{14}$ (1$\cdot CH_2Cl_2 \cdot 1/2C_6H_{14}$)

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with dichloromethane and hexanes of solvation. The $Re_2Cl_5(PCy_2H)_3$ molecule (Fig. 1) belongs to a large class of 1,3,6-isomers [9] having two phosphine groups *trans* to each other on one of the metal atoms. The P–Re–P angle is 164.4(1)° and Re–P distances are averaged to 2.451(5) Å. The Re–Re bond of 2.223(1) Å is typical for corresponding dirhenium molecules with a bond order of 3.5 [10]. The $Re_2Cl_5(PCy_2H)_3$ molecule exhibits the highest deviation from the eclipsed geometry among 1,3,6-$Re_2Cl_5(PR_3)_3$ structures with the average P–Re–Re–Cl torsion angle as high as 12.0(2)°.

3.2. $[Bu^n_4N][Re_2(\mu\text{-}PCy_2)_3Cl_6] \cdot 3/4(CH_3)_2CO$ (2$\cdot 3/4(CH_3)_2CO$) and $[Bu^n_4N][Re_2(\mu\text{-}PPh_2)_3Cl_6]$ (3)

Compound **2** conforms to the monoclinic space group $P2_1$ with two crystallographically independent dirhenium anions $[Re_2(PCy_2)_3Cl_6]^-$ and two tetra-*n*-butylammonium cations in the unit cell. In the dirhenium anion (Fig. 2) two rhenium(IV) atoms are bridged by three dicyclohexylphosphido groups. Three terminal chloride ligands complete the coordination sphere of each metal center, thus defining the core structure as a face-sharing bioctahedral dirhenium complex.

The two complexes **2** and **3** obtained here are close analogues. The structure of **3** was not completely refined because the severe disorder of the tetra-*n*-butylammonium cations in $[Bu^n_4N][Re_2(\mu\text{-}PPh_2)_3Cl_6]$ (**3**) could not be modeled[1]. However, all geometric characteristics of the dirhenium anion $[Re_2(\mu\text{-}PPh_2)_3Cl_6]^-$ in **3** (Fig. 3) are reliable. Comparison of structural parameters of the two $[Re_2(\mu\text{-}PR_2)_3Cl_6]^-$ ions where R = Cy or Ph, revealed a very close similarity of two complexes (Table 3). For example, the average Re–P distances and the Re–P–Re angles are 2.390(4) and 2.380(6) Å and 60.39(9) and 61.5(2)° for **2** and **3**, respectively. These two anions are also closely similar to the analogous anion with diethylphosphido groups, $[Re_2(\mu\text{-}PEt_2)_3Cl_6]^-$, reported by us [2]: Re–Re, 2.406 Å; Re–P–Re, 61.3°.

Table 2
Selected bond distances (Å), angles (°) and torsion angles (°) for 1,3,6-$Re_2Cl_5(PCy_2H)_3$ (**1**)

Bond distances			
Re(1)–Re(2)	2.223(1)		
Re(1)–P(1)	2.447(5)	Re(2)–P(3)	2.428(4)
Re(1)–P(2)	2.478(5)	Re(2)–Cl(3)	2.333(5)
Re(1)–Cl(1)	2.345(4)	Re(2)–Cl(4)	2.313(4)
Re(1)–Cl(2)	2.323(4)	Re(2)–Cl(5)	2.350(4)
Bond angles			
P(1)–Re(1)–P(2)	164.4(1)		
P(1)–Re(1)–Cl(1)	85.2(2)	P(3)–Re(2)–Cl(3)	81.5(2)
P(1)–Re(1)–Cl(2)	87.2(2)	P(3)–Re(2)–Cl(4)	90.2(2)
P(2)–Re(1)–Cl(1)	91.5(2)	P(3)–Re(2)–Cl(5)	159.7(2)
P(2)–Re(1)–Cl(2)	86.0(2)	Cl(3)–Re(2)–Cl(5)	87.7(2)
Cl(1)–Re(1)–Cl(2)	141.8(2)	Cl(3)–Re(2)–Cl(4)	142.5(2)
		Cl(4)–Re(2)–Cl(5)	88.1(2)
Torsion angles			
P(1)–Re(1)–Re(2)–Cl(3)	15.5(2)		
P(2)–Re(1)–Re(2)–Cl(4)	8.5(2)		
Cl(1)–Re(1)–Re(2)–P(3)	10.9(2)		
Cl(2)–Re(1)–Re(2)–Cl(5)	12.9(2)		

Table 3
Averaged bond distances (Å) and angles in $[Bu^n_4N][Re_2(\mu\text{-}PCy_2)_3Cl_6]$ (**2**) and $[Bu^n_4N][Re_2(\mu\text{-}PPh_2)_3Cl_6]$ (**3**)

	2	**3**
Bond distances		
Re–Re	2.4049(8)	2.435(1)
Re–P	2.390(4)	2.380(6)
Re–Cl	2.430(3)	2.413(5)
Bond angles		
Re–P–Re	60.39(9)	61.5(2)
P–Re–P	96.9(1)	96.2(2)
Re–Re–P	59.80(9)	59.3(1)
Cl–Re–Cl	84.1(1)	83.9(2)
Re–Re–Cl	129.35(9)	129.5(2)
P–Re–Cl	170.8(1)	170.8(2)
	89.1(1)	89.7(2)

Table 4
Selected bond distances (Å) and Angles (°) for $[Re_2(\mu\text{-}PPh_2)_2(PPh_2H)_2Cl_6]^{2-}$ anion in (**4**)

Bond distances			
Re(1)–Re(2)	2.7494(7)		
Re(1)–P(1)	2.312(2)	Re(2)–P(1)	2.313(2)
Re(1)–P(2)	2.322(2)	Re(2)–P(2)	2.321(2)
Re(1)–P(3)	2.398(2)	Re(2)–P(4)	2.395(2)
Re(1)–Cl(1)	2.507(2)	Re(2)–Cl(4)	2.521(2)
Re(1)–Cl(2)	2.438(2)	Re(2)–Cl(6)	2.441(2)
Re(1)–Cl(3)	2.502(2)	Re(2)–Cl(5)	2.494(2)
Bond angles			
P(1)–Re(1)–P(2)	107.23(7)	P(1)–Re(2)–P(2)	107.21(7)
P(1)–Re(1)–P(3)	90.48(7)	P(1)–Re(2)–P(4)	90.70(7)
P(2)–Re(1)–P(3)	95.93(7)	P(2)–Re(2)–P(4)	95.30(7)
P(1)–Re(1)–Cl(1)	83.67(7)	P(1)–Re(2)–Cl(4)	83.48(7)
P(1)–Re(1)–Cl(2)	99.89(7)	P(1)–Re(2)–Cl(6)	99.54(7)
P(1)–Re(1)–Cl(3)	162.68(7)	P(1)–Re(2)–Cl(5)	162.88(7)
P(2)–Re(1)–Cl(1)	168.62(7)	P(2)–Re(2)–Cl(4)	168.91(7)
P(2)–Re(1)–Cl(2)	93.27(7)	P(2)–Re(2)–Cl(6)	93.43(7)
P(2)–Re(1)–Cl(3)	89.14(7)	P(2)–Re(2)–Cl(5)	89.14(7)
P(3)–Re(1)–Cl(1)	87.05(7)	P(4)–Re(2)–Cl(4)	87.35(7)
P(3)–Re(1)–Cl(2)	163.47(7)	P(4)–Re(2)–Cl(6)	163.96(7)
P(3)–Re(1)–Cl(3)	82.04(7)	P(4)–Re(2)–Cl(5)	82.56(7)
Cl(1)–Re(1)–Cl(2)	81.39(7)	Cl(4)–Re(2)–Cl(5)	80.51(7)
Cl(1)–Re(1)–Cl(3)	80.38(7)	Cl(4)–Re(2)–Cl(6)	81.63(6)
Cl(2)–Re(1)–Cl(3)	84.40(7)	Cl(5)–Re(2)–Cl(6)	84.14(7)
Re(2)–Re(1)–P(1)	53.54(5)	Re(1)–Re(2)–P(1)	53.51(5)
Re(2)–Re(1)–P(2)	53.69(5)	Re(1)–Re(2)–P(2)	53.70(5)
Re(2)–Re(1)–P(3)	95.34(5)	Re(1)–Re(2)–P(4)	95.10(5)
Re(2)–Re(1)–Cl(1)	137.11(5)	Re(1)–Re(2)–Cl(4)	136.90(5)
Re(2)–Re(1)–Cl(2)	101.17(5)	Re(1)–Re(2)–Cl(6)	100.91(5)
Re(2)–Re(1)–Cl(3)	142.44(5)	Re(1)–Re(2)–Cl(5)	142.54(5)
Re(1)–P(1)–Re(2)	72.94(6)	Re(1)–P(2)–Re(2)	72.62(6)

3.3. $[Bu^n_4N]_2[Re_2(\mu\text{-}PPh_2)_2(PPh_2H)_2Cl_6]\cdot 31/2(CH_3)_2CO$ ($4\cdot 31/2(CH_3)_2CO$)

Compound **4** crystallizes in the triclinic $P\bar{1}$ space group with one dirhenium anion, $[Re_2(\mu\text{-}PPh_2)_2(PPh_2H)_2Cl_6]^{2-}$, and two tetra-*n*-butylammonium cations in the asymmetric unit. Each anion consists of two rhenium(III) atoms bridged by two diphenylphosphido groups with the Re–P distances averaged to 2.317(2) Å (Fig. 4). There are also one terminal neutral diphenylphosphine group (the average Re–P distance is 2.397(2) Å) and three chloride ligands (average Re–Cl, 2.484(2) Å) on each metal center, which define its structure as an ESBO dirhenium(III) complex. For the anion in **4** the rhenium–rhenium separation is 2.7494(7) Å, which is close to the value of 2.7551(6) Å in the dirhenium(III) ESBO $Re_2(\mu\text{-}PEt_2)_2Cl_4(PEt_2H)_4$ [2] and indicative of the presence of the Re–Re bond. In contrast to the small diethylphosphine ligand [11], two bulky PPh_2H probably can not

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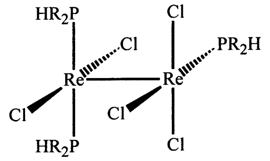
[1] Crystal data for $[Bu^n_4N][Re_2(\mu\text{-}PPh_2)_3Cl_6]$ (**3**): triclinic $P\bar{1}$, $a = 13.717(5)$ Å, $b = 20.374(6)$ Å, $c = 20.575(4)$ Å, $\alpha = 106.48(2)°$, $\beta = 95.02(2)°$, $\gamma = 100.31(2)°$, $V = 5366(3)$ Å^3, $Z = 4$, $\rho_{calc.} = 1.712$ g cm^{-3}, $T = 138$ K, empirical absorption correction (0.3090–0.9918 transmission coefficient), full-matrix refinement on F^2 (Enraf–Nonius CAD-4S, SHELXL-93), R_1 (on F_0) = 0.1061 for 504 parameters and 11305 unique data ($I > 2\sigma(I)$), $R_2 = 0.1288$ for all 13 955 data.

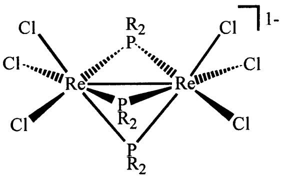
be accommodated at one Re^{III} center in **4**, so the compositions of these two ESBO complexes are different.

4. Discussion

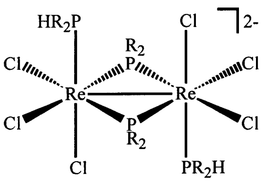
In the course of studying reactions of the $[Re_2Cl_8]^{2-}$ ion with monodentate phosphines [1–3] we have found that benzene is an interesting reaction medium in which disproportionation reactions proceed affording both oxidized and reduced rhenium products [3]. We previously studied the reaction of $[Re_2Cl_8]^{2-}$ with the small cone-angle secondary phosphine, PEt_2H. Both dirhenium(II,II) and dirhenium(IV,IV) products were isolated from the same reaction as a result of disproportionation [2]:



1



2, 3



4

Chart 1. Schematic representation of the structures reported here.

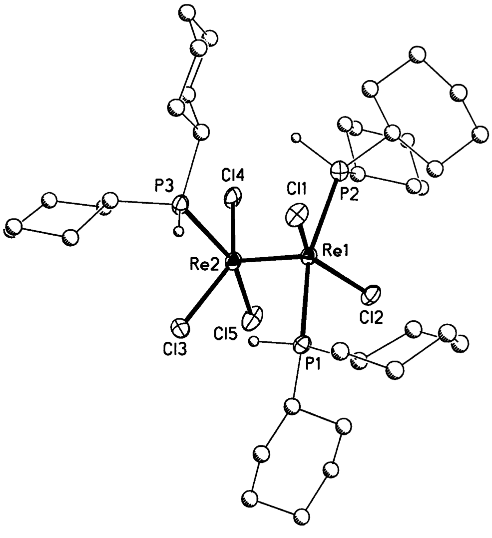


Fig. 1. A perspective drawing of 1,3,6-$Re_2Cl_5(PCy_2H)_3$ (**1**). Atoms are represented by thermal ellipsoids at the 35% probability level. Carbon atoms and hydrogen atoms attached to the phosphorus atoms are shown as spheres of arbitrary radii. Hydrogen atoms of cyclohexyl groups are omitted.

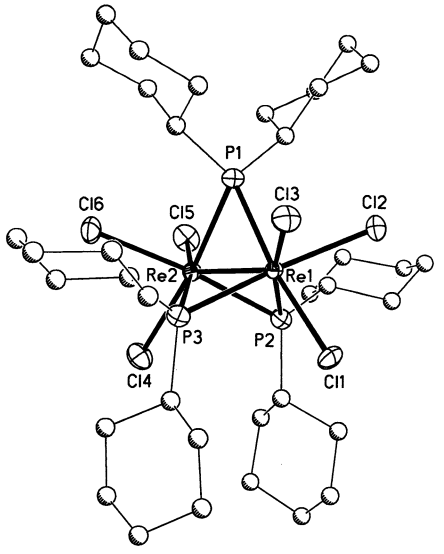


Fig. 2. A perspective drawing of the $[Re_2(\mu\text{-}PCy_2)_3Cl_6]^-$ in **2**. Atoms are represented by thermal ellipsoids at the 35% probability level. Carbon atoms are shown as spheres of arbitrary radii. Hydrogen atoms are omitted.

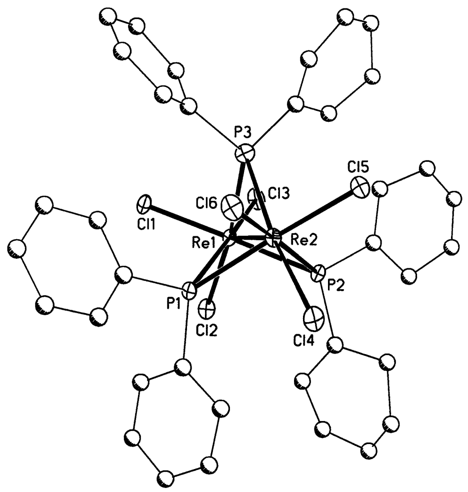


Fig. 3. A perspective drawing of the $[Re_2(\mu\text{-}PPh_2)_3Cl_6]^-$ in **3**. Atoms are represented by thermal ellipsoids at the 35% probability level. Carbon atoms are shown as spheres of arbitrary radii. Hydrogen atoms are omitted.

$$2[Bu^n_4N]_2[Re_2Cl_8] + 10PEt_2H$$
$$\rightarrow Re_2Cl_4(PEt_2H)_4 + [Bu^n_4N][Re_2(\mu\text{-}PEt_2)_3Cl_6]$$
$$+ 3\ [Bu^n_4N]Cl + 3\ [PEt_2H_2]Cl \qquad (1)$$

Schematically this disproportionation process can be written as: $2Re_2^{6+} \rightarrow Re_2^{4+} + Re_2^{8+}$.

The unusual ESBO compound, $Re_2(\mu\text{-PEt}_2)_2Cl_4(PEt_2H)_4$, containing both terminal phosphines and phosphido bridges, was also obtained by carrying out a reaction in benzene under mild conditions [2]:

$$[Bu_4^nN]_2[Re_2Cl_8] + 8PEt_2H$$
$$\rightarrow Re_2(\mu\text{-PEt}_2)_2Cl_4(PEt_2H)_4 + 2[Bu_4^nN]Cl + 2[PEt_2H_2]Cl \qquad (2)$$

It was proposed that the overall disproportionation process proceeds through this intermediate:

$$2Re_2(\mu\text{ -PEt}_2)_2Cl_4(PEt_2H)_4 + 2Cl^- + [PEt_2H_2]^+$$
$$\rightarrow Re_2Cl_4(PEt_2H)_4 + [Re_2(\mu\text{-PEt}_2)_3Cl_6]^- + 6PEt_2H \qquad (3)$$

From the reaction of $[Re_2Cl_8]^{2-}$ with PCy_2H in benzene at room temperatures we have also isolated both reduced and oxidized dirhenium products from one pot:

$$3\ [Bu_4^nN]_2[Re_2Cl_8] + 12PCy_2H$$
$$\rightarrow 2Re_2Cl_5(PCy_2H)_3\ (\mathbf{1}) + [Bu_4^nN][Re_2Cl_6(PCy_2)_3]\ (\mathbf{2})$$
$$+ 5[Bu_4^nN]Cl + 3[PCy_2H_2]Cl \qquad (4)$$

This disproportionation reaction can be schematically presented as $3\ Re_2^{6+} \rightarrow 2\ Re_2^{5+} + Re_2^{8+}$. The difference from the PEt_2H reaction is that the reduced product in reaction (4) contains the Re_2^{5+} core rather than the Re_2^{4+} core, while the oxidized product is still of the $[Re_2(\mu\text{-PR}_2)_3Cl_6]^{1-}$ type, typical for secondary phosphines. In reactions with tertiary phosphines we found the same Re_2^{5+} reduced products, but different oxidized products, all monomeric rhenium(IV) complexes of the $ReCl_4(PR_3)_2$ type [3], since a tertiary phosphine cannot easily give rise to R_2P bridges.

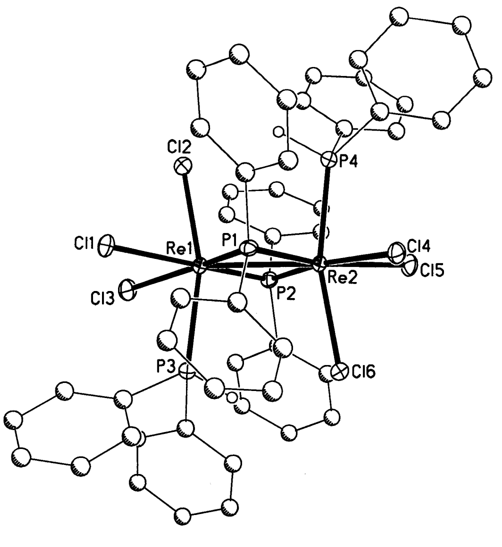


Fig. 4. A perspective drawing of the $[Re_2(\mu\text{-PPh}_2)_2(PPh_2H)_2Cl_6]^{2-}$ in **4**. Atoms are represented by thermal ellipsoids at the 35% probability level. Carbon atoms and hydrogen atoms attached to the phosphorus atoms are shown as spheres of arbitrary radii. Hydrogen atoms of phenyl groups are omitted.

As crystals of **1** and **2** have distinctively different colors, they were separated manually and characterized individually. Both compounds are air-stable, but they lose solvents of crystallization so quickly at room temperature that accurate chemical analysis data could not be obtained.

For the system $[Re_2Cl_8]^{2-}$–PPh_2H, the reaction was performed in toluene at reflux conditions affording analogous to **2** the dirhenium(IV) complex with diphenylphosphido bridges, $[Bu_4^nN][Re_2(\mu\text{-PPh}_2)_3Cl_6]$ (**3**). We did not isolate the reduced dirhenium complex from this system, but we believe there is a disproportionation reaction analogous to that shown in eq. (4).

In an effort to detect intermediates in the present reactions, we studied the transformations in the system $[Re_2Cl_8]^{2-}$–PPh_2H in dichloromethane under mild experimental conditions and short reaction times. For diphenylphosphine we found an interesting and novel dirhenium(III) ESBO compound, $[Bu_4^nN]_2[Re_2(\mu\text{-PPh}_2)_2(PPh_2H)_2Cl_6]$ (**4**), which is formed at an early stage:

$$[Bu_4^nN]_2[Re_2Cl_8] + 6PPh_2H$$
$$\rightarrow [Bu_4^nN]_2[Re_2Cl_6(PPh_2)_2(PPh_2H)_2] + 2[PPh_2H_2]Cl \qquad (5)$$

We believe this ESBO complex may be an intermediate in the disproportionation process, according to the following reaction, to give the dirhenium(IV) complex **2** or **3** and the reduced dirhenium(II,III) species (for R = Ph, Cy):

$$3[Bu_4^nN]_2[Re_2Cl_6(PR_2)_2(PR_2H)_2]$$
$$\rightarrow [Bu_4^nN][Re_2Cl_6(\mu\text{ -PR}_2)^4_3] + 2Re_2Cl_5(PR_2H)_3$$
$$+ 5[Bu_4^nN] + 3PR_2^- + 2\ Cl^- \qquad (6)$$

In conclusion, our present results again provide evidence in favor of a disproportionation mechanism for the reaction system $[Re_2Cl_8]^{2-}$–PR_2H when the solvent itself, e.g. benzene, toluene, hexane and dichloromethane, cannot be the actual reducing agent.

5. Supplementary material

Crystallographic data (excluding structure factors) for $\mathbf{1}\cdot CH_2Cl_2\cdot 1/2C_6H_{14}$, $\mathbf{2}\cdot 3/4(CH_3)_2CO$, and $\mathbf{4}\cdot 31/2(CH_3)_2CO$ have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 166881, 166882 and 166883. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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References

[1] F.A. Cotton, E.V. Dikarev, M.A. Petrukhina, J. Am. Chem. Soc. 119 (1997) 12541.

[2] F.A. Cotton, E.V. Dikarev, M.A. Petrukhina, Inorg. Chem. 37 (1998) 6035.

[3] F.A. Cotton, E.V. Dikarev, M.A. Petrukhina, Inorg. Chem. 38 (1999) 3384.

[4] J. Pflugrath, A. Messerschmitt, MADNES, Munich Area Detector (New EEC) System, version EEC 11/9/89, with enhancements by Enraf-Nonius Corp., Delft, The Netherlands. A description of MADNES appears in: A. Messerschmitt, J. Pflugrath, J. Appl. Crystallogr. 20 (1987) 306.

[5] (a) W. Kabsch, J. Appl. Crystallogr. 21 (1988) 67;
(b) W. Kabsch, J. Appl. Crystallogr. 21 (1988) 916.

[6] R.H. Blessing, Acta Crystallogr. A51 (1995) 33.

[7] SHELXTL V.5; Siemens Industrial Automation Inc.: Madison, WI, 1994.

[8] G.M. Sheldrick, in: H.D. Flack, L. Parkanyi, K. Simon (Eds.), Crystallographic Computing 6, Oxford University Press, Oxford, UK, 1993, p. 111.

[9] (a) F.A. Cotton, A.C. Price, K. Vidyasagar, Inorg. Chem. 29 (1990) 5143;
(b) F.A. Cotton, E.V. Dikarev, Inorg. Chem. 32 (1995) 3809;
(c) F.A. Cotton, S.C. Haefner, A.P. Sattelberger, Inorg. Chem. 35 (1996) 1831;
(d) F.A. Cotton, E.V. Dikarev, M.A. Petrukhina, Inorg. Chem. 37 (1998) 1949.

[10] F.A. Cotton, R.A. Walton, Multiple Bonds Between Metal Atoms, second ed., Oxford University Press, Oxford, UK, 1993.

[11] C.A. Tolman, Chem. Rev. 77 (1977) 313.