Note

The structural characterization of $Re_2Cl_4(\mu\text{-dcpm})_2$ ($dcpm = Cy_2PCH_2PCy_2$) and a new crystallographic form of $Re_2Cl_4(\mu\text{-dppm})_2$ ($dppm = Ph_2PCH_2PPh_2$)

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Abstract

The single crystal X-ray structures of the triply bonded complexes $Re_2Cl_4(\mu\text{-dcpm})_2$ (**1**) ($dcpm = Cy_2PCH_2PCy_2$) and a new crystal form of $Re_2Cl_4(\mu\text{-dppm})_2$ (**2**) ($dppm = Ph_2PCH_2PPh_2$) have been determined and are compared with literature data for other complexes of this type. Complexes **1** and **2** both possess staggered rotational geometries. Complex **1** has Re–Re distances of 2.2256(4) and 2.2267(4) Å for two crystallographically independent molecules. Complex **2** also has two independent molecules in the asymmetric unit, one of which is normal with Re–Re = 2.2497(4) Å, whereas the other exhibits a twofold orientational disorder for the Re–Re unit (distances 2.2368(5) Å and 2.231(4) Å for the major (90%) and minor (10%) forms respectively). © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The triply bonded dirhenium(II) complex $Re_2Cl_4(\mu\text{-dppm})_2$ ($dppm = Ph_2PCH_2PPh_2$) was first reported almost 25 years ago [1] and its solid state structure was established in 1985 [2].
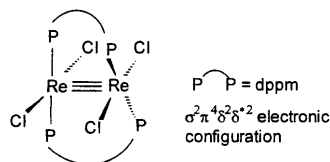
Since then it has been used as a useful synthon for carrying out an extensive reaction chemistry involving rhenium–rhenium multiple bonds, e.g. see Ref. [3]. Changing the diphosphine ligand in a complex of the type $Re_2Cl_4(\mu\text{-PP})_2$ ($PP = R_2P\text{–}A\text{–}PR_2$; $A = CH_2$, NH, $C=CH_2$, etc.) could bring about variations in these reactivity patterns. Moreover, the possibility of generating a different structure type cannot be ruled out. This has prompted us to synthesize complexes that contain other bridging diphosphine ligands and to study their reactivities. These include $Re_2Cl_4(\mu\text{-dppa})_2$ ($dppa = Ph_2NHPPh_2$) [4], $Re_2Cl_4(\mu\text{-dcpm})_2$ ($dcpm = Cy_2PCH_2PCy_2$) [5] and, most recently, $Re_2Cl_4(\mu\text{-dppE})_2$ ($dppE = Ph_2PC(=CH_2)PPh_2$) [6].

The solid-state structures of all these complexes have been reported with the exception of the dcpm derivative. Although we published the synthesis and reactions of this complex some time back [5,7], a structural analysis was not performed as we were unable to obtain a suitable single crystal for an X-ray diffraction study. In the present report we describe the structural characterization of the complex $Re_2Cl_4(\mu\text{-dcpm})_2$ (**1**) and also the solid state structure of a new crystal form of $Re_2Cl_4(\mu\text{-dppm})_2$ (**2**).

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2. Experimental

2.1. Starting materials

A sample of crystalline $Re_2Cl_4(\mu\text{-dcpm})_2$ (**1**) was obtained directly from the reaction mixture upon refluxing $cis\text{-}Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(H_2O)_2$ with dcpm in ethanol in the presence of a pine boiling stick under a positive pressure of N_2 [5]. Single crystals of **1** were carefully removed from the surface of the pine boiling stick after a reaction time of 2 h and used for the X-ray diffraction studies. A nearly quantitative yield of $Re_2Cl_4(\mu\text{-dppm})_2$ (**2**) was obtained by refluxing an ethanol solution containing $cis\text{-}Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(H_2O)_2$ and dppm for 18 h under similar conditions [8]. Single crystals suitable for X-ray diffraction studies were harvested directly from the reaction mixture.

2.2. X-ray crystallography

Data collections were performed at 173 ± 1 K with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on a Nonius Kappa CCD diffractometer. Lorentz and polarization corrections were applied to the data sets. The crystallographic data for **1** and **2** are given in Table 1.

The structures were solved using the structure solution program PATTY in DIRDIF92 [9]. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were placed in calculated positions according to idealized geometries with C–H = 0.95 Å and $U(H) = 1.3U_{eq}(C)$. They were included in the refinement but constrained to ride on the

atom to which they are bonded. An empirical absorption correction using SCALEPACK [10] was applied. The final refinements were performed by the use of the program SHELXL-97 [11].

2.2.1. $Re_2Cl_4(\mu\text{-dcpm})_2$ (**1**)

A dark red plate-shaped crystal having approximate dimensions $0.25 \times 0.25 \times 0.13$ mm was selected for the data collection. A total of 47 632 reflections were collected in the range $4.0 < \theta < 27.9°$, of which 24 637 were unique. Four of the carbon atoms of one of the cyclohexyl rings (C(121)–C(126)) were found to be disordered over two positions with half occupancies. These half atom pairs are labeled C(12A) and C(12B), C(13A) and C(13B), C(15A) and C(15B), and C(16A) and C(16B). All non-hydrogen atoms were refined with anisotropic thermal parameters. A total of 24 634 reflections were used in the refinement. However, only reflections with $F_o^2 > 2\sigma|F_o^2|$ were used in calculating R. The final cycle of refinement included 1117 variable parameters and converged with unweighted agreement factor $R = 0.051$. The largest remaining peak for **1** in the final difference Fourier had a height of 1.84 e- Å^{-3}.

2.2.2. $Re_2Cl_4(\mu\text{-dppm})_2$ (**2**)

A dark red needle crystal having approximate dimensions of $0.40 \times 0.20 \times 0.17$ mm was selected for the data collection. A total of 61 334 reflections were collected in the range of $4.0 < \theta < 27.5°$, of which 20 736 were unique. All non-hydrogen atoms were refined with anisotropic thermal parameters. A total of 20 246 reflections were used in the refinement. However, only reflections with $F_o^2 > 2\sigma|F_o^2|$ were used in calculating R. The final cycle of refinement included 1100 variable parameters and converged with unweighted agreement factor $R = 0.050$. The largest remaining peak for **2** in the final difference Fourier had a height of 2.09 e- Å^{-3}.

The important intramolecular bond distances and angles for the structures of **1** and **2** are given in Tables 2 and 3.

3. Results and discussion

The successful solution of the single crystal X-ray structure determination of $Re_2Cl_4(\mu\text{-dcpm})_2$ (**1**) shows that this complex is very similar to other complexes of the type $Re_2Cl_4(\mu\text{-PP})_2$ (PP = dppm [2], dppa [4] or dppE [6]) in which the bidentate phosphine ligand PP bridges the two Re atoms in an intramolecular fashion. Several structures have been reported recently that contain dcpm bound in a chelating mode in mononuclear complexes or bridging two metal centers in bimetallic species [12–14]. An ORTEP representation [15] of the
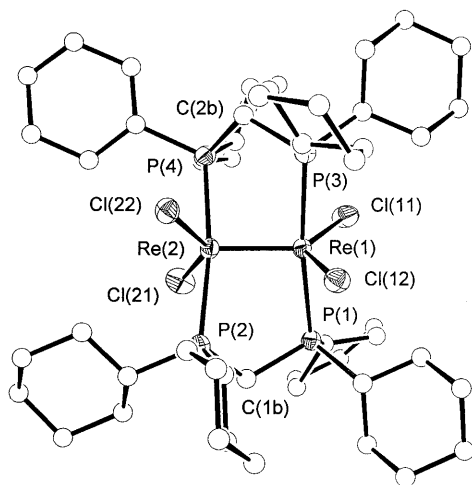
Table 1
Crystallographic data for $Re_2Cl_4(\mu\text{-dcpm})_2$ (**1**) and $Re_2Cl_4(\mu\text{-dppm})_2$ (**2**)

	1	**2**
Chemical formula	$C_{50}H_{92}Cl_4P_4Re_2$	$C_{50}H_{44}Cl_4P_4Re_2$
Formula weight	1331.40	1283.02
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
a (Å)	15.5493(4)	20.6843(3)
b (Å)	17.7957(5)	20.1674(5)
c (Å)	22.1000(7)	23.0724(6)
α (°)	98.3218(16)	90
β (°)	110.4447(15)	95.4177(14)
γ (°)	90.0303(17)	90
V (Å^3)	5661.2(6)	9581.6(6)
Z	4	8
ρ_{calcd} (g cm^{-3})	1.562	1.779
μ(Mo Kα) (mm^{-1})	4.664	5.509
Trans. factors (min/max)	0.41, 0.56	0.33, 0.38
R (F_o)[a]	0.051	0.050
$R_w(F_o^2)$[b]	0.110	0.104
GOF	1.033	1.024

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$.
[b] $R_w = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

Fig. 1. ORTEP [15] representation of the structure of $Re_2Cl_4(\mu\text{-dcpm})_2$ (1) with the important atoms labeled. The thermal ellipsoids are drawn at the 40% probability level except for the carbon atoms of the dcpm ligands, which are circles of arbitrary radius.

Table 2
Important bond distances (Å) and bond angles (°) for the complex $Re_2Cl_4(\mu\text{-dcpm})_2$ (1)[a]

Distances			
Re(1)–Re(2)	2.2256(4)	Re(2)–Cl(21)	2.3816(19)
Re(1)–Cl(12)	2.3766(17)	Re(2)–Cl(22)	2.3831(18)
Re(1)–Cl(11)	2.3840(18)	Re(2)–P(4)	2.4359(19)
Re(1)–P(1)	2.4598(19)	Re(2)–P(2)	2.4437(19)
Re(1)–P(3)	2.4674(19)		
Angles			
Re(2)–Re(1)–Cl(12)	112.67(5)	Re(1)–Re(2)–Cl(21)	112.98(6)
Re(2)–Re(1)–Cl(11)	115.03(5)	Re(1)–Re(2)–Cl(22)	108.83(5)
Cl(12)–Re(1)–Cl(11)	132.26(7)	Cl(21)–Re(2)–Cl(22)	138.17(7)
Re(2)–Re(1)–P(1)	94.02(4)	Re(1)–Re(2)–P(4)	94.13(5)
Cl(12)–Re(1)–P(1)	89.46(6)	Cl(21)–Re(2)–P(4)	91.53(7)
Cl(11)–Re(1)–P(1)	89.01(7)	Cl(22)–Re(2)–P(4)	84.46(7)
Re(2)–Re(1)–P(3)	93.08(5)	Re(1)–Re(2)–P(2)	93.88(4)
Cl(12)–Re(1)–P(3)	87.29(6)	Cl(21)–Re(2)–P(2)	83.50(7)
Cl(11)–Re(1)–P(3)	88.49(7)	Cl(22)–Re(2)–P(2)	94.84(6)
P(1)–Re(1)–P(3)	172.87(6)	P(4)–Re(2)–P(2)	171.75(6)

[a] Data given for one of the two independent molecules in the asymmetric unit. Full data are available as supplementary material. Numbers in parentheses are esds in the least significant digits.

structure of 1 is shown in Fig. 1. Two independent molecules of $Re_2Cl_4(\mu\text{-dcpm})_2$ were found in the asymmetric unit. These have very similar structural parameters, so data for only one of these molecules (molecule 1) are listed in Table 2. The Re–Re distances for molecules 1 and 2 are 2.2256(4) Å and 2.2267(4) Å respectively, values that are similar to the literature data for $Re_2Cl_4(\mu\text{-dppm})_2$ (2.234(3) Å) [2], $Re_2Cl_4(\mu\text{-dppa})_2$ (2.2417(5) Å) [4] and $Re_2Cl_4(\mu\text{-dppE})_2$ (2.2448(5) Å) [6]. The Re–Cl and Re–P distances span

quite narrow ranges and these resemble closely the data for analogous $Re_2Cl_4(\mu\text{-PP})$ complexes [2,4,6]. The staggered rotational geometry of this molecule is evident from the values for the torsional angles Cl(11)–Re(1)–Re(2)–Cl(21), Cl(12)–Re(1)–Re(2)–Cl(22), P(1)–Re(1)–Re(2)–P(2) and P(3)-Re(1)–Re(2)–P(4), which are 44.0°, 43.1°, 37.8° and 40.3° respectively. The analogous values for molecule 2 are 42.5°, 42.2°, 39.2° and 39.0° respectively.

In our original structural characterization of the complex $Re_2Cl_4(\mu\text{-dppm})_2$ (2) [2], X-ray-quality crystals were eventually obtained, after considerable effort, from a dichloromethane–hexane solvent mix. The complex itself was obtained in crude form by the reaction of $Re_2Cl_6(P^nBu_3)_3$ with dppm in reagent-grade acetone [2,16]. In the present study, single crystals of 2 were obtained directly from the reaction of cis-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(H_2O)_2$ with dppm in ethanol [8], a procedure similar to that used to prepare $Re_2Cl_4(\mu\text{-dcpm})_2$ [5]. Preliminary data collection on these crystals of 2 showed that they were of a different crystal form than that reported in the earlier study [2]. Accordingly, a full structure determination was carried out.

The batch of crystals studied earlier [2] and those obtained in the present work both belong to the space group $P2_1/n$. Although both sets of crystals contain $Re_2Cl_4(\mu\text{-dppm})_2$, the cell volumes are different. A more compact cell (9581.6(6) Å³ for $Z = 8$) is observed for the crystal form that is reported here, compared with the one that was reported earlier [2] (i.e. 5776(4) Å³ for $Z = 4$). Two independent molecules were observed in the asymmetric unit of the crystal chosen in the most recent study. One of these (molecule 1) is quite normal and essentially identical with the molecules present in other $Re_2Cl_4(\mu\text{-PP})_2$ structures. An ORTEP representation [15] of this molecule is given in Fig. 2 and its

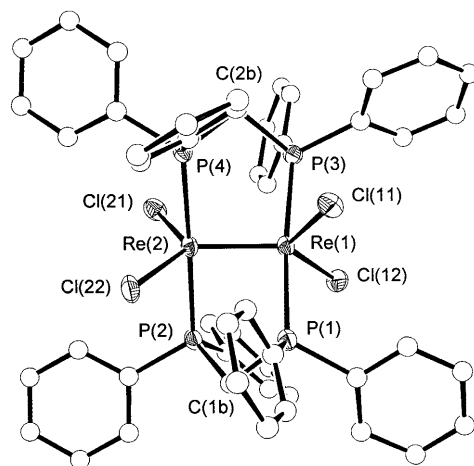Fig. 2. ORTEP [15] representation of the structure of molecule 1 in the asymmetric unit of $Re_2Cl_4(\mu\text{-dppm})_2$ (2) with the important atoms labeled. The thermal ellipsoids are drawn at the 40% probability level except for the carbon atoms of the dppm ligands, which are circles of arbitrary radius.

structural parameters are summarized in Table 3. The distance Re(1)–Re(2) is 2.2497(4) Å, a value that is similar to the one reported earlier (2.234(3) Å) [2]. The torsional angles Cl(11)–Re(1)–Re(2)–Cl(22), Cl(12)–Re(1)–Re(2)–Cl(21), P(1)–Re(1)–Re(2)-P(2) and P(3)–Re(1)–Re(2)–P(4) are 54.2°, 51.0°, 45.5° and 45.5° respectively.

The second molecule (molecule 2) in the asymmetric unit of **2**, like molecule 1, possesses a staggered rotational geometry, but it differs in exhibiting a twofold orientational disorder. The ORTEP representation [15] of this disorder is shown in Fig. 3, with only the Re, Cl, P

Table 3
Important bond distances (Å) and bond angles (°) for molecule 1 present in crystals of $Re_2Cl_4(\mu\text{-dppm})_2$ **(2)**[a]

| Distances			
Re(1)–Re(2)	2.2497(4)	Re(2)–Cl(21)	2.356(2)
Re(1)–Cl(12)	2.3495(19)	Re(2)–Cl(22)	2.362(2)
Re(1)–Cl(11)	2.3585(19)	Re(2)–P(2)	2.4341(19)
Re(1)–P(1)	2.418(2)	Re(2)–P(4)	2.4366(19)
Re(1)–P(3)	2.422(2)		
Angles			
Re(2)–Re(1)–Cl(12)	118.70(5)	Re(1)–Re(2)–Cl(21)	117.02(5)
Re(2)–Re(1)–Cl(11)	118.88(5)	Re(1)–Re(2)–Cl(22)	118.13(6)
Cl(12)–Re(1)–Cl(11)	122.40(7)	Cl(21)–Re(2)–Cl(22)	124.83(8)
Re(2)–Re(1)–P(1)	92.19(5)	Re(1)–Re(2)–P(2)	90.44(5)
Cl(12)–Re(1)–P(1)	89.04(7)	Cl(21)–Re(2)–P(2)	94.77(7)
Cl(11)–Re(1)–P(1)	90.50(7)	Cl(22)–Re(2)–P(2)	83.62(7)
Re(2)–Re(1)–P(3)	92.97(5)	Re(1)–Re(2)–P(4)	90.71(5)
Cl(12)–Re(1)–P(3)	90.60(7)	Cl(21)–Re(2)–P(4)	86.84(7)
Cl(11)–Re(1)–P(3)	84.89(7)	Cl(22)–Re(2)–P(4)	93.71(7)
P(1)–Re(1)–P(3)	174.30(7)	P(2)–Re(2)–P(4)	177.33(7)

[a] Numbers in parentheses are esds in the least significant digits.
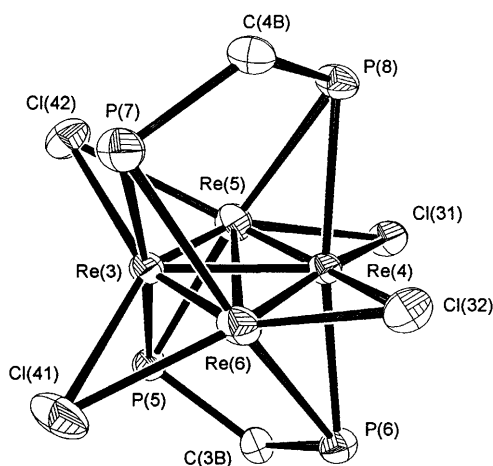
Fig. 3. ORTEP [15] representation of the structure of molecule 2 in the asymmetric unit of $Re_2Cl_4(\mu\text{-dppm})_2$ to reveal the twofold orientational disorder involving the dirhenium units Re(3)–Re(4) (90% occupancy) and Re(5)–Re(6) (10% occupancy), and showing the connectivity to the coordinated ligand atoms Cl and P. The thermal ellipsoids are drawn at the 50% probability level.

and methylene C atoms displayed for simplicity. Both dirhenium units (Re(3)–Re(4) and Re(5)–Re(6)) share the same sets of Cl and P atoms but have quite different occupancies, with the major form (Re(3)–Re(4)) being 90% and the minor form (Re(5)–Re(6)) only 10%. The distances Re(3)–Re(4) and Re(5)–Re(6) are 2.2368(5) Å and 2.231(4) Å respectively. Although the parameters for the Re–Cl and Re–P bonds involving Re(3)–Re(4) are normal, with Re–Cl and Re–P distances in the ranges 2.360(2)–2.384(2) Å and 2.418(2)–2.464(2) Å respectively, some of the corresponding distances involving Re(5)–Re(6) are longer by up to 0.1–0.2 Å. This may reflect the fact that the Cl and P atom positions for the minor form (only 10% occupancy) do not match exactly those of the major form, but are not resolvable as separate atomic positions.

Although the highly basic dcpm ligand forms a complex of the type $Re_2Cl_4(\mu\text{-PP})_2$, to date we have been unable to synthesize an analogous complex with $Me_2PCH_2PMe_2$ (dmpm), which has similar basicity to dcpm. The isolated complex was found to be $Re_2Cl_4(\mu\text{-dmpm})_3$ [17]. The nature of the products from the reactions of $Re_2(\mu\text{-O}_2CCH_3)_2Cl_4(H_2O)_2$ with diphosphine ligands depend on the steric requirements of the ligands, and on their basicity. Owing to the smaller size of the dmpm, it is possible to accommodate three such ligands in the primary coordination sphere of the $[Re_2]^{4+}$ unit. Interestingly, the reaction of $Ph_2PC(CH_3)_2PPh_2$ (2,2-dppp) with $Re_2(\mu\text{-O}_2CCH_3)_2Cl_4(H_2O)_2$ yields the mononuclear complex $ReCl_2(\zeta^2\text{-}(2,2\text{-dppp-pdm})_2$ in high yield [18]. Apparently, the presence of two methyl groups at the carbon atom reduces the bite angle of the ligand and this can favor the disruption of the Re≡Re bond and conversion to a six-coordinate mononuclear complex. Studies with this particular phosphine ligand are continuing.

4. Supplementary material

Tables giving full details for the crystal data and data collection parameters, atomic positional parameters, anisotropic thermal parameters, bond distances and bond angles for compounds **1** and **2** are available on request from the author (RAW).

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