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The syntheses and structures of salts of the octachlorodirhenate(III) and octachlorodiosmate(III) anions with the 1,2-bis(triphenylphosphonium)ethane cation

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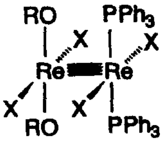
Abstract—The reactions of *cis*-$Re_2(O_2CCH_3)_2Cl_4(py)_2$ or $(n\text{-}Bu_4N)_2Re_2Cl_8$ with PR_3 (R = Cy or Ph) in refluxing 1,2-dichloroethane afford the bis-phosphonium salts $(R_3PCH_2CH_2PR_3)Re_2Cl_8$; the crystal structure of the derivative where R = Ph shows that this is only the second example of a salt of the $[Re_2Cl_8]^{2-}$ anion in which a 3-fold orientational disorder of the Re—Re units is encountered. A cation exchange reaction between $(Ph_3PCH_2CH_2PPh_3)Cl_2$ and $(n\text{-}Bu_4N)_2Os_2Cl_8$ affords $(Ph_3PCH_2CH_2PPh_3)Os_2Cl_8$, which possesses an Os—Os bond distance of 2.1896(3) Å and is the second example of a crystal structure of a $[Os_2Cl_8]^{2-}$ salt in which a fully staggered rotational geometry is present. © 1997 Elsevier Science Ltd

Keywords: octachlorodirhenate(III) anion; octachlorodiosmate(III) anion; bis(triphenylphosphonium)ethane cation; metal–metal multiple bonds.

The novel mixed halide–alkoxide complexes of the type $Re_2X_4(OR)_2(PPh_3)_2$ (X = Cl, Br; R = Me, Et, *n*-Pr, *i*-Pr) possess the asymmetric Re(IV)–Re(II) mixed-valence structure represented in **I** [1,2]. These complexes are the products of the reactions of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2X_4L_2$ (X = Cl, Br; L = H_2O, DMF, DMSO) with PPh_3 in the appropriate refluxing alcohol [1,2], in which an intramolecular disproportionation reaction has occurred at a multiple metal–metal bond [3] without any change in the formal M—M bond order. In order to investigate and develop the chemistry of these prototype molecules in more detail, we are currently looking at ways by which the symmetric isomers of structure type **II** might be accessed. To this end, we are carrying out a comparative study of the reactions of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2X_4L_2$ (L = H_2O, py) with PPh_3 and PCy_3 (Cy = cyclohexyl), in order to establish whether there is a dependence of the reaction pathway upon the basicity and steric bulk of the phosphine, and to ascertain the influence of reaction solvent upon the reaction course. We have found that when 1,2-dichloroethane is used as the reaction solvent, in the absence of alcohol, the salts $(R_3PCH_2CH_2PR_3)Re_2Cl_8$ (R = Ph, Cy) are produced. The properties of these complexes are reported along with the single crystal X-ray structures of $(Ph_3PCH_2CH_2PPh_3)Re_2Cl_8$ and its analogous diosmium(III) salt.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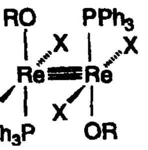
II

EXPERIMENTAL

Starting materials

Phosphine ligands (PPh_3 and PCy_3) and all common solvents were used as received from commercial sources. The salts $(n\text{-}Bu_4N)_2Re_2Cl_8$ and $(n\text{-}Bu_4N)_2Os_2Cl_8$ were prepared as described in the literature [4,5],

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while *cis*-$Re_2(O_2CCH_3)_2Cl_4(py)_2$ was obtained by a slight modification of the literature procedure [2]. Samples of the salt $(Ph_3PCH_2CH_2PPh_3)Cl_2$ were prepared by refluxing a solution of PPh_3 in 1,2-$C_2H_4Cl_2$ for 3 days. The ^1H NMR spectrum of a solution of this compound in DMSO-d_6 consisted of multiplets at δ +7.90 and +7.74 (Ph, 30 H) and δ +3.99 (CH_2CH_2, 4H). This spectrum agrees closely with that reported for the analogous bromide salt [6]. The $^{31}P\{^1H\}$ NMR spectrum showed a sharp singlet at δ +26.3. The analogous cyclohexylphosphine derived salt $(Cy_3PCH_2CH_2PCy_3)Cl_2$ was obtained by refluxing a solution of PCy_3 in 1,2-$C_2H_4Cl_2$ for 3 days. Its ^1H NMR spectrum in DMSO-d_6 showed resonances at δ +1.36(m,br), +1.50(m), +1.67(s,br), +1.78(s,br), +1.88(s), +1.92(s), and +2.82(m), due to the cyclohexyl groups, and at δ +2.65 (m, CH_2CH_2, 4H). The $^{31}P\{^1H\}$ NMR spectrum consisted of a sharp singlet at δ +35.9.

Reaction procedures

All reactions were performed under an atmosphere of dry nitrogen, and all solvents were deoxygenated prior to use unless otherwise specified.

(*a*) *Reactions of* cis-$Re_2(O_2CCH_3)_2Cl_4(py)_2$ *with monodentate phosphines in* 1,2-*dichloroethane*. (i) $(Cy_3PCH_2CH_2PCy_3)Re_2Cl_8\cdot 2.5C_2H_4Cl_2$ (**1**). A mixture of *cis*-$Re_2(O_2CCH_3)_2Cl_4(py)_2$ (0.10 g, 0.13 mmol) and PCy_3 (0.18 g, 0.64 mmol) was refluxed in 15 cm^3 of 1,2-dichloroethane for 3 days. The resulting blue crystalline product was filtered off, and washed with 1,2-dichloroethane and then diethyl ether; yield 0.153 g (79%). Found: C, 34.7; H, 5.7; Cl, 30.8. Calc. for $C_{43}H_{80}Cl_{13}P_2Re_2$ (i.e. $(Cy_3PCH_2CH_2PCy_3)Re_2Cl_8\cdot 2.5C_2H_4Cl_2$): C, 34.6; H, 5.4; Cl, 30.9%. The presence of lattice solvent molecules was confirmed by ^1H NMR spectroscopy (δ +3.87 in DMSO-d_6 with an integration corresponding to 2–3 molecules of 1,2-$C_2H_4Cl_2$).

This same compound was obtained upon using $(n\text{-}Bu_4N)_2Re_2Cl_8$ in place of *cis*-$Re_2(O_2CCH_3)_2Cl_4(py)_2$ in the above reaction; isolated yield 31%.

(ii) $(Ph_3PCH_2CH_2PPh_3)Re_2Cl_8$ (**2**). A reaction similar to that described in (a)(i), between *cis*-$Re_2(O_2CCH_3)_2Cl_4(py)_2$ (0.10 g, 0.13 mmol) and PPh_3 (0.10 g, 0.38 mmol) afforded the title complex as blue crystals; yield 0.050 g (32%). Found: C, 37.8; H, 2.8; Cl, 23.4. Calc. for $C_{38}H_{34}Cl_8P_2Re_2$: C, 37.7; H, 2.8; Cl, 23.5%.

Samples of **2** could be obtained in appreciably higher yields by substituting $(n\text{-}Bu_4N)_2Re_2Cl_8$ for *cis*-$Re_2(O_2CCH_3)_2Cl_4(py)_2$; isolated yield 80%.

(*b*) *cation exchange reaction of* $(n\text{-}Bu_4N)_2Os_2Cl_8$ *with* $(Ph_3PCH_2CH_2PPh_3)Cl_2$. *The synthesis of* $(Ph_3PCH_2CH_2PPh_3)Os_2Cl_8$ (**3**). A sample of $(n\text{-}Bu_4N)_2Os_2Cl_8$ (0.067 g, 0.058 mmol) was dissolved in 4 cm^3 of dichloromethane and a solution of $(Ph_3PCH_2CH_2PPh_3)Cl_2$ (0.040 g, 0.064 mmol) in ethanol (4 cm^3) carefully layered on top of the former solution. The reaction vessel was stoppered to prevent evaporation. Over a period of one week a crop of green crystals of $(Ph_3PCH_2CH_2PPh_3)Os_2Cl_8$ separated; these were filtered off, washed with ethanol and diethyl ether, and dried; yield 0.051 g (72%). Found: C, 35.8; H, 2.8. Calc. for $C_{39}H_{36}Cl_{10}Os_2P_2$ (i.e. $(Ph_3PCH_2CH_2PPh_3)Os_2Cl_8\cdot CH_2Cl_2$): C, 36.0; H, 2.8%. Although the presence of a molecule of CH_2Cl_2 solvent in the crystalline lattice was supported by the ^1H NMR spectrum of this product (δ +5.73 in DMSO-d_6), the crystal selected for an X-ray diffraction analysis was not found to contain a molecule of solvent. Accordingly, this composition must reflect an average stoichiometry, in which varying amounts of solvent are probably present in different crystals.

Physical measurements

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded with the use of a GE QE-300 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated DMSO-d_6 solvent, while phosphorus resonances were referenced externally to a sample of H_3PO_4. Elemental microanalyses were performed by Dr H. D. Lee of the Purdue University Microanalytical Laboratory.

X-ray crystallography

Single crystals of **2** and **3** suitable for diffraction analysis were obtained directly from the reaction vessels. A blue plate of **2** and green plate of **3**, having approximate dimensions of 0.24 × 0.22 × 0.10 mm and 0.40 × 0.28 × 0.14 mm, respectively, were mounted on glass fibers in a random orientation. The data were collected at 295 K on an Enraf-Nonius CAD4 computer-controlled diffractometer with graphite-monochromatized Mo-K_α radiation. The basic crystallographic parameters for these two crystals are listed in Table 1. The cell constants were based on 25 reflections in the range $17 < \theta < 21°$, measured by the computer-controlled diagonal slit method of centering. Three standard reflections were measured after every 5000 s of beam time during data collection and there were no systematic variations in intensity. Lorentz and polarization corrections were applied to both data sets. An empirical absorption correction, based on the method of Walker and Stuart [7], was also applied, but no corrections for extinction were made. Calculations were performed on an AlphaServer 2100 computer using the Enraf-Nonius structure determination package (MolEN) [8].

Both **2** and **3** crystallized in the monoclinic crystal system; the space group was determined to be $P2_1/n$ and $P2_1/c$, respectively. The structures were solved by a combination of direct methods (SIR92 [9] for **2** and DIRDIF92 [10] for **3**) and difference Fourier syntheses. During the course of the analysis of **2**, the

Table 1. Crystallographic data for $(Ph_3PCH_2CH_2PPh_3)Re_2Cl_8$ (**2**) and $(Ph_3PCH_2CH_2PPh_3)Os_2Cl_8$ (**3**)

	2	**3**
Formula	$Re_2Cl_8P_2C_{38}H_{34}$	$Os_2Cl_8P_2C_{38}H_{34}$
fw	1208.67	1216.67
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	9.189(2)	10.4927(17)
b (Å)	21.2123(17)	19.320(2)
c (Å)	20.898(4)	20.383(4)
β (°)	95.412(16)	99.338(13)
V (Å^3)	4055(2)	4077(2)
Z	4	4
T (°C)	22	22
λ (Mo-K_α) (Å)	0.71073	0.71073
ρ_{calc} (g cm^{-3})	1.981	1.983
μ (Mo-K_α) (mm^{-1})	6.690	6.876
Transm. coeff. (max, min)	0.89–0.61	0.84–0.51
R^a	0.033	0.034
R_w^b	0.036	0.045
GOF	0.317	1.485

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

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

Re—Re unit was found to be disordered. A disorder model involving three sets of fractional Re—Re units was established and satisfactorily refined to occupancies of $M_{Re(1)/Re(2)} = 0.766$, $M_{Re(1a)/Re(2a)} = 0.178$, $M_{Re(1b)/(2b)} = 0.056$, with $M_{Re(1)/Re(2)} + M_{Re(1a)/Re(2a)} + M_{Re(1b)/(2b)} = 1$. These three sets of Re—Re units were perpendicular to one another. The structure of compound **3** was solved without disorder. For both structures, hydrogen atoms were calculated with C—H = 0.95 Å and U = 1.3 $U(C)_{eq}$ and added to the structure factor calculations, but their positions were not refined. The structures were refined in full-matrix least squares, where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(|F_o|)$. All non-hydrogen atoms were refined anisotropically. Corrections for anomalous scattering were applied to these atoms [11]. The final residues were $R = 0.033$ and $R_w = 0.036$ with GOF = 0.317 for **2**, and $R = 0.034$ and $R_w = 0.045$ with GOF = 1.485 for **3**. The highest peaks in the final difference Fourier maps of **2** and **3** were 0.70 and 2.43 e/Å^3, respectively.

RESULTS AND DISCUSSION

The reactions between *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_4L_2$ (L = H_2O or py) and PPh_3 in refluxing alcohols (ROH) proceed according to eq. (1), to afford dirhenium alkoxides with the mixed-valence structure **I** [1,2].

$$cis\text{-}Re_2(\mu\text{-}O_2CCH_3)_2Cl_4L_2 + 2PPh_3 + 2ROH \rightarrow$$
$$Re_2Cl_4(OR)_2(PPh_3)_2 + 2CH_3CO_2H + 2L. \quad (1)$$

Our attempts to prepare the analogous PCy_3 complexes by a similar procedure to that shown in eq. (1) were not successful; pure, characterizable rhenium-containing products were not isolated. However, when the alcohol solvents were replaced by 1,2-dichloroethane, the reaction between *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(py)_2$ and Cy_3P afforded a blue microcrystalline product, **1**, which exhibited very low solubility in both polar and non-polar solvents, thereby limiting its characterization. It was, however, slightly soluble in DMF and DMSO; the ^{1}H NMR spectrum of a solution of **1** in DMSO-d_6 showed a complex set of cyclohexyl resonances at δ +1.35(m,br), +1.49(m), +1.68(s,br), +1.79(s,br), +1.88(s), +1.92(s) and +2.78(m,br), and an additional multiplet at δ +2.58, while the $^{31}P\{^1H\}$ spectrum consisted of a sharp singlet at δ +35.9.

When the reaction between PPh_3 and *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(py)_2$ was carried out in refluxing 1,2-dichloroethane, a blue solid, **2**, was also obtained. Like **1**, complex **2** also possesses very low solubility, although DMSO-d_6 again proved adequate as a solvent for NMR spectral characterizations. The ^{1}H NMR spectrum of **2** showed phenyl resonances at δ +7.90 and +7.73, and a multiplet at δ +3.93, while the $^{31}P\{^1H\}$ NMR spectrum had a sharp singlet at δ +26.3. While the $^{31}P\{^1H\}$ spectrum of **2** is very similar to that of $Re_2Cl_6(PPh_3)_2$ in DMSO-d_6 (δ +26.2), it differs from the ^{1}H NMR spectrum of $Re_2Cl_6(PPh_3)_2$ which shows only a single complex multiplet at δ +7.55 [12], thereby establishing that it is not another structural isomer of $Re_2Cl_6(PPh_3)_2$.

Since we recognized that the NMR spectral properties of **1** and **2** are essentially identical in all respects with those of samples of the diphosphonium salts $(Cy_3PCH_2CH_2PCy_3)Cl_2$ and $(Ph_3PCH_2CH_2PPh_3)Cl_2$, which were isolated from the reactions of Cy_3P and Ph_3P with refluxing 1,2-dichloroethane (see Experimental for further details), we concluded that **1** and **2** were in reality the complexes $(Cy_3PCH_2CH_2PCy_3)Re_2Cl_8$ and $(Ph_3PCH_2CH_2PPh_3)Re_2Cl_8$, respectively. This conclusion was confirmed by the successful solution of the crystal structure of **2** (*vide infra*). Accordingly, the formation of **1** and **2** occurs through the reaction shown in eq. (2), where the 1,2-dichloroethane solvent reacts with PR_3 to form $(R_3PCH_2CH_2PR_3)Cl_2$, which provides both the excess of chloride necessary to displace the acetate ligands and the diphosphonium cations to stabilize the $[Re_2Cl_8]^{2-}$ and $CH_3CO_2^-$ anions that are formed.

$$\begin{aligned} &cis\text{-}Re_2(O_2CCH_3)_2Cl_4L_2 + 4PR_3 + 2C_2H_4Cl_2 \\ &\quad \rightarrow (R_3PCH_2CH_2PR_3)Re_2Cl_8 \\ &\quad + (R_3PCH_2CH_2PR_3)(O_2CCH_3)_2 + 2L. \qquad (2) \end{aligned}$$

The crystal structure of **2** confirms the presence of the $[Ph_3PCH_2CH_2PPh_3]^{2+}$ cation and the $[Re_2Cl_8]^{2-}$ anion. This is only the second example of a salt of $[Re_2Cl_8]^{2-}$ anion in which 3-fold orientational disorder of the Re—Re units is encountered [13], while the Cambridge Data Base lists only two other structures containing the $[Ph_3PCH_2CH_2PPh_3]^{2+}$ dication [14,15]. An ORTEP representation of the $[Re_2Cl_8]^{2-}$ anion showing the 3-fold disorder is given in Fig. 1, while key bond distances and angles are listed in Table 2. The occupancies for Re(1)—Re(2), Re(1a)—Re(2a) and Re(1b)—Re(2b) are 76.6, 17.8 and 5.6%, respectively; for $(Et_4N)_2Re_2Cl_8$ they are 67, 17 and 16% [13]. The distance Re(1)—Re(2) of 2.2221(6) Å is typical for an eclipsed, quadruply bonded $[Re_2Cl_8]^{2-}$ anion [16], while the Re—Cl distances and Re—Re—Cl and Cl—Re—Cl angles are normal. The four torsional Cl—Re—Re—Cl angles, which define the essentially eclipsed rotational geometry for the major orientation Re(1)—Re(2), are 6.3(1), 7.4(1), 5.1(1) and 6.6(1)°. The $[Ph_3PCH_2CH_2PPh_3]^{2+}$ cation has a geometry similar to that reported in a previously determined structure [14(b)], with a torsional angle P(1)—C(1)—C(2)—P(2) of 148.9(5)° defining the rotational geometry about the C—C bond.

To establish the ease of isolating other dimetal salts of the $[Ph_3PCH_2CH_2PPh_3]^{2+}$ dication, we prepared the green crystalline salt $(Ph_3PCH_2CH_2PPh_3)Os_2Cl_8$, **3**, in high yield by the reaction of $(Ph_3PCH_2CH_2PPh_3)Cl_2$ with $(n\text{-}Bu_4N)_2Os_2Cl_8$ in ethanol/dichloromethane. The structure of **3** was also determined by X-ray crystallography. Figure 2 gives an ORTEP representation of the structure of the $[Os_2Cl_8]^{2-}$ anion, while important bond distances and angles are presented in Table 3. Unlike the $[Re_2Cl_8]^{2-}$ anion, wherein which an eclipsed rotational geometry is a consequence of the δ-bond and enhances the opportunity for crystallographic orientational disorder, the electron-rich triply bonded $[Os_2Cl_8]^{2-}$ anion ($\sigma^2\pi^4\delta^2\delta^{*2}$ ground state electronic configuration) can assume any rotational geometry [17–

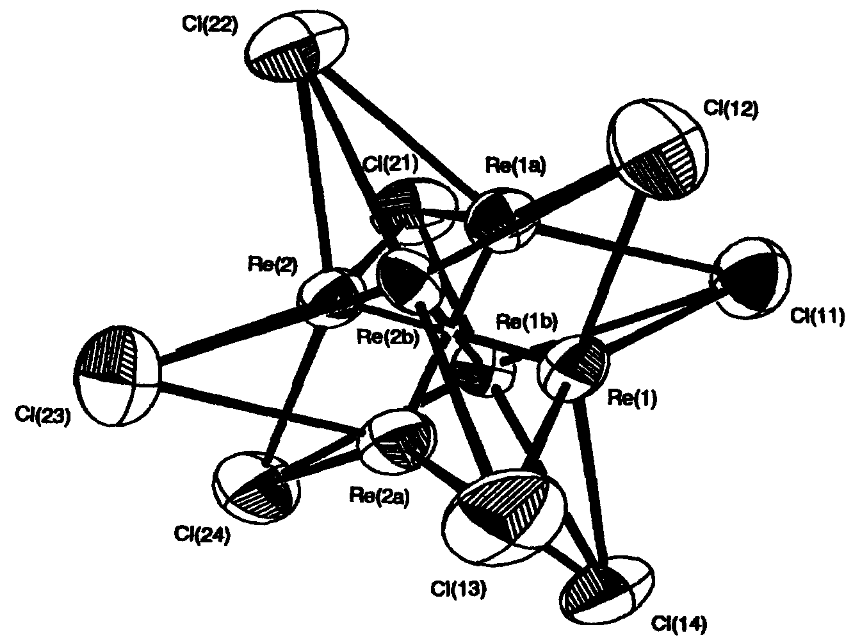

Fig. 1. ORTEP representation of the structure of the $[Re_2Cl_8]^{2-}$ anion as present in the salt $(Ph_3PCH_2CH_2PPh_3)Re_2Cl_8$ (**2**) showing the 3-fold orientational disorder of the Re—Re units. The thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected bond distances (Å) and angles (°) for (Ph$_3$PCH$_2$CH$_2$PPh$_3$)Re$_2$Cl$_8$ (**2**)^{a,b}

Re(1)—Re(2)	2.2221(6)	P(1)—C(1)	1.814(8)
Re(1a)—Re(2a)	2.217(3)	P(1)—C(111)	1.780(8)
Re(1b)—Re(2b)	2.220(7)	P(1)—C(121)	1.786(8)
Re(1)—Cl(11)	2.322(2)	P(1)—C(131)	1.782(8)
Re(1)—Cl(12)	2.347(3)	P(2)—C(2)	1.821(8)
Re(1)—Cl(13)	2.294(3)	P(2)—C(211)	1.790(8)
Re(1)—Cl(14)	2.346(2)	P(2)—C(221)	1.787(8)
Re(2)—Cl(21)	2.340(2)	P(2)—C(231)	1.800(8)
Re(2)—Cl(22)	2.347(2)	C(1)—C(2)	1.545(11)
Re(2)—Cl(23)	2.338(2)		
Re(2)—Cl(24)	2.326(2)		
Re(2)—Re(1)—Cl(11)	104.66(7)	Re(1)—Re(2)—Cl(21)	102.62(6)
Re(2)—Re(1)—Cl(12)	102.79(6)	Re(1)—Re(2)—Cl(22)	102.93(6)
Re(2)—Re(1)—Cl(13)	104.05(7)	Re(1)—Re(2)—Cl(23)	101.89(7)
Re(2)—Re(1)—Cl(14)	101.99(7)	Re(1)—Re(2)—Cl(24)	104.84(6)
Cl(11)—Re(1)—Cl(12)	86.60(9)	Cl(21)—Re(2)—Cl(22)	86.84(8)
Cl(11)—Re(1)—Cl(13)	151.29(10)	Cl(21)—Re(2)—Cl(23)	155.47(9)
Cl(11)—Re(1)—Cl(14)	87.36(9)	Cl(21)—Re(2)—Cl(24)	86.69(8)
Cl(12)—Re(1)—Cl(13)	86.94(9)	Cl(22)—Re(2)—Cl(23)	88.79(9)
Cl(12)—Re(1)—Cl(14)	155.22(9)	Cl(22)—Re(2)—Cl(24)	152.22(9)
Cl(13)—Re(1)—Cl(14)	86.90(9)	Cl(23)—Re(2)—Cl(24)	86.02(9)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

[b] Distances and angles involving the minor Re$_2$ orientations Re(1a)—Re(2a) and Re(1b)—Re(2b) are available as supplementary information.

Table 3. Selected bond distances (Å) and angles (°) for (Ph$_3$PCH$_2$CH$_2$PPh$_3$)Os$_2$Cl$_8$ (**3**)^{a}

Os(1)—Os(2)	2.1896(3)	P(1)—C(1)	1.809(8)
Os(1)—Cl(1)	2.3355(14)	P(1)—C(111)	1.778(8)
Os(1)—Cl(2)	2.3180(15)	P(1)—C(121)	1.802(8)
Os(1)—Cl(3)	2.3185(16)	P(1)—C(131)	1.796(8)
Os(1)—Cl(4)	2.3217(15)	P(2)—C(2)	1.810(8)
Os(2)—Cl(5)	2.3350(15)	P(2)—C(211)	1.772(8)
Os(2)—Cl(6)	2.3073(17)	P(2)—C(221)	1.796(9)
Os(2)—Cl(7)	2.3399(16)	P(2)—C(231)	1.805(8)
Os(2)—Cl(8)	2.3063(16)	C(1)—C(2)	1.535(11)
Os(2)—Os(1)—Cl(1)	103.92(4)	Os(1)—Os(2)—Cl(5)	104.91(4)
Os(2)—Os(1)—Cl(2)	103.65(4)	Os(1)—Os(2)—Cl(6)	107.67(4)
Os(2)—Os(1)—Cl(3)	102.80(5)	Os(1)—Os(2)—Cl(7)	102.90(4)
Os(2)—Os(1)—Cl(4)	105.44(4)	Os(1)—Os(2)—Cl(8)	103.43(5)
Cl(1)—Os(1)—Cl(2)	86.87(6)	Cl(5)—Os(2)—Cl(6)	85.53(6)
Cl(1)—Os(1)—Cl(3)	153.27(6)	Cl(5)—Os(2)—Cl(7)	152.18(6)
Cl(1)—Os(1)—Cl(4)	86.37(6)	Cl(5)—Os(2)—Cl(8)	86.87(6)
Cl(2)—Os(1)—Cl(3)	86.06(6)	Cl(6)—Os(2)—Cl(7)	85.54(7)
Cl(2)—Os(1)—Cl(4)	150.90(6)	Cl(6)—Os(2)—Cl(8)	148.90(6)
Cl(3)—Os(1)—Cl(4)	87.39(6)	Cl(7)—Os(2)—Cl(8)	87.31(6)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

20]. The structure of **3** can be compared most closely to that of (n-Bu$_4$N)$_2$Os$_2$Cl$_8$ [18], which is the only other salt of this anion to have been structurally characterized in which a staggered, non-disordered, rotational geometry is present. The Os—Os distance for **3** of 2.1896(3) Å is similar to that of 2.182(1) Å for (n-Bu$_4$N)$_2$Os$_2$Cl$_8$ [18]. The Os—Cl distances and Os—Os—Cl and Cl—Os—Cl angles for these two structures are also very similar. The torsional angles Cl(1)—Os(1)—Os(2)—Cl(6), Cl(2)—Os(1)—Os(2)—Cl(7), Cl(3)—Os(1)—Os(2)—Cl(8) and Cl(4)—Os(1)—Os(2)—Cl(5), which can be used to define the

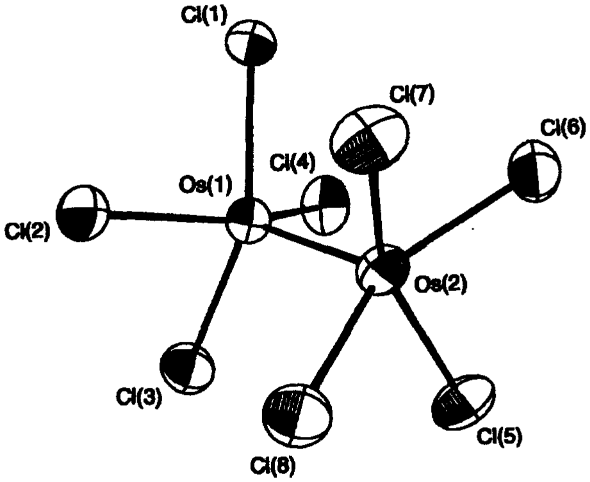

Fig. 2. ORTEP representation of the structure of the $[Os_2Cl_8]^{2-}$ anion as present in the salt $(Ph_3PCH_2CH_2PPh_3)Os_2Cl_8$, **3**. The thermal ellipsoids are drawn at the 50% probability level.

rotational geometry of **3** (see Fig. 2), are 44.4(1), 54.1(1), 43.7(1) and 53.2(1)°, respectively. The $[Ph_3PCH_2CH_2PPh_3]^{2+}$ cation of **3** is structurally very similar to that present in the structure of **2** (see Table 3); the torsional angle P(1)—C(1)—C(2)—P(2) is 143.4(5)° and very similar to that of **2**.

There are three additional reports on structures of salts of the $[Os_2Cl_8]^{2-}$ anion in the literature [17,19,20] but in these instances a 2-fold orientation disorder is present. In the cases of $(Ph_3MeP)_2Os_2Cl_8$ [20] and the brown form of $(PPN)_2Os_2Cl_8$ (PPN = $[Ph_2PNPPh_2]^+$) [19], the torsional angles are 0° (by crystallographic symmetry) and the two Os—Os units in the 2-fold disorder have Os—Os distances which span the range 2.208(1)–2.213(1) Å; the lengthening relative to the Os—Os distances in **3** can be attributed to increased Cl $\cdots$ Cl repulsions in the eclipsed structures. A green form of $(PPN)_2Os_2Cl_8$ has the rather unusual combination of a staggered rotational geometry and a 2-fold orientational disorder [19].

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