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# Syntheses and structures of *trans*-[ReX(CO)(Ph₂PCH₂PPh₂)₂] (X = Cl, OReO₃), including a rhenium(I)–rhenium(VII) complex *

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## Abstract

Reduction of $Re_2Cl_{10}$ or $NH_4ReO_4$ by $NaBH_4$ in the presence of $Ph_2PCH_2PPh_2$, dppm, and CO provides a simple route to the complexes *trans*-[ReX(CO)(dppm)₂], **1**, X = Cl or **2**, X = ReO₄ respectively. Both complexes have been characterised by an X-ray diffraction study. In each complex the $Ph_2PCH_2PPh_2$ ligands adopt the chelating bonding mode and the coordination geometry around the rhenium(I) centre is distorted octahedral. Complex **2** contains both rhenium(I) and rhenium(VII) centres, and a Re–O–ReO₃ linkage with $Re^I$–O and $Re^{VII}$–O distances of 2.207(3) Å and 1.754(3) Å, respectively.

## 1. Introduction

Complexes of rhenium(I) containing chelating dppe ligands (dppe = $Ph_2PCH_2CH_2PPh_2$) have been extensively studied and include interesting compounds such as [Re(N₂)Cl(dppe)₂] [1] but the analogous compounds of dppm (dppm = $Ph_2PCH_2PPh_2$) have received much less attention [2]. This may be due partly to the lack of a convenient synthetic method. We now describe a simple one-pot synthesis of the title compounds from the easily available starting materials $Re_2Cl_{10}$ and $NH_4ReO_4$ and the characterisation of the products by X-ray crystallography and spectroscopic methods. The complex *trans*-[Re(OReO₃)(CO)(dppm)₂] is of particular interest, since it contains rhenium atoms in both oxidation states (I) and (VII).

## 2. Results and discussion

The synthesis of *trans*-[ReCl(CO)(dppm)₂], **1**, was previously carried out by refluxing [ReCl(CO)₅] with dppm for long periods, but the reported yield was only 5–16% [2a]. Compound **1** has also been prepared by the reaction of [Bu₄N]₂[ReCl₆] with dppm in boiling DMF under an inert atmosphere [2b]. We report below an easy synthesis of **1** by reduction of [Re₂Cl₁₀] with NaBH₄ in the presence of CO and dppm. In addition, it is shown that the related perrhenate derivative *trans*-[Re(OReO₃)(CO)(dppm)₂], **2**, can be obtained by reduction of ReO₄⁻ with NaBH₄ under similar conditions. In each case, the reaction is carried out by addition of six molar equivalents of NaBH₄ to a suspension of dppm and Re₂Cl₁₀ or NH₄ReO₄ in ethanol under a carbon monoxide atmosphere; the reaction is complete in a few hours at room temperature and the product is formed in good yield. The product in each case was identified by an X-ray crystal structure study.

The molecular structure of **1** (Fig. 1) involves a distorted octahedral geometry around the rhenium(I) centre, with the two chelating dppm ligands forming

four equatorial Re-P bonds. In crystals of **1** the asymmetric unit contains two chemically identical molecules. One of these is partially disordered, with the chloride and carbonyl ligands of the *trans*-Cl-Re-CO unit displaying a 61:39 occupancy of the two coordination sites on opposite sides of the ReP$_4$ plane. The bond lengths and angles for **1** are listed in Table 1. The molecular structure of **2** (Fig. 2), characterized by the bond lengths and angles shown in Table 2, can be derived from that of **1** by replacing the chloride with a perrhenate ligand. In both **1** and **2** the four-membered ReP$_2$C rings are subject to severe angular distortions (Tables 1 and 2) similar to those usually observed in transition metal complexes containing chelating dppm ligands [3]. The steric bulk of the ligands and the geometrical constraints imposed by formation of the ReP$_2$C rings result in substantial distortions from idealised octahedral geometry around the rhenium(I) centres; these distortions, evident from the bond angles listed in Table 1 and 2, are larger in **2**, in accordance with the higher steric requirements of the ReO$_4^-$ than of the Cl$^-$ ion. The Re-Cl, Re-C and Re-P bond lengths in **1** and **2** reveal no unexpected features.

In **2** the perrhenate ion is weakly coordinated to the rhenium(I) centre to form a Re$^I$-ORe$^{VII}$O$_3$ fragment in which the angle at the bridging oxygen atom is 167.1(2)°. The Re(I)-O bond of 2.207(3) Å is much longer than the Re(V)-OReO$_3$ bonds of 2.031(6)-2.096(9) Å in the octahedral rhenium(V) complexes [ReOI$_2$(OReO$_3$)(PPh$_3$)$_2$], **3**, [ReOI$_2$(OReO$_3$)(PPh$_3$)-

(OPPh$_3$)], **4**, and [Re$_2$O($\mu$-O)$_2$(C$_5$Me$_5$)$_2$(OReO$_3$)$_2$], **5** [4,5]. Within the coordinated ReO$_4^-$ ion in **2**, the Re(VII)-O bond involving the bridging oxygen [1.754(3) Å] is about 0.05 Å longer than the other three Re-O bonds [1.695(5)-1.703(4) Å]. This feature has also been observed in other crystallographically characterized perrhenate complexes [4-7].

Particularly interesting in the molecular structure of **2** is the presence of both Re$^I$ and Re$^{VII}$ centres. In the Re-O-ReO$_3$ bridge the Re$^I$-O bond is about 0.45 Å longer than the Re$^{VII}$-O bond (see above), reflecting the difference of six in the oxidation states and of two in the coordination numbers of the metal centres. In the complexes **3** to **5**, in which the metal atoms have the same coordination geometries as in **2**, but have oxidation states differing by two units only, the Re$^V$-O bonds are only about 0.23-0.30 Å longer than the Re$^{VII}$-O bonds involving the bridging oxygen.

The spectroscopic data for **1** (Table 3) were fully consistent with its molecular structure and also with those for *trans*-[ReCl(CO)(dppm)$_2$] reported previously [2a]. Similarly, complex **2** gave a singlet in the $^{31}$P{$^1$H} NMR spectrum, with a chemical shift consistent with chelating dppm, and an "AB" pattern in the $^1$H NMR caused by the non-equivalent CH$^a$H$^b$P$_2$ protons. In the IR spectrum, CO-stretching band of **2** was observed at 1862 cm$^{-1}$, at a slightly higher frequency than that for **1** (1841, 1831 cm$^{-1}$; two bands resulting from solid-state splitting are as expected from the X-ray structure described above) and from the spectra
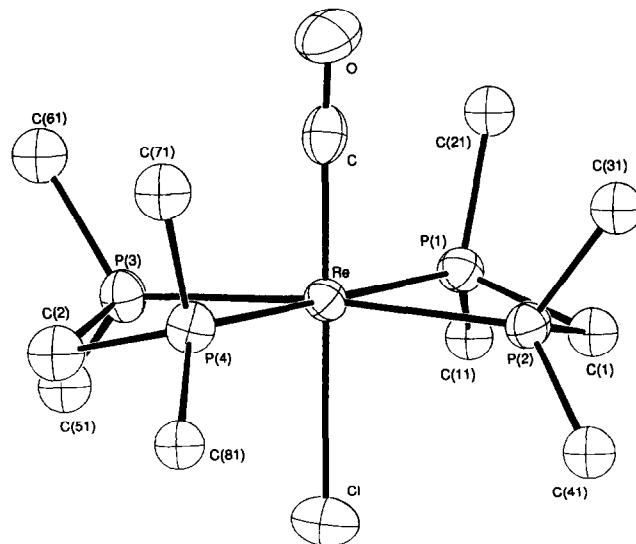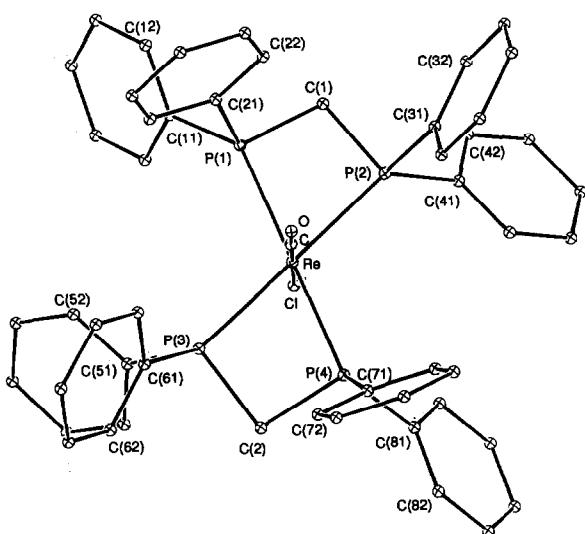


Fig. 1. (a) A view of the ordered molecule of [ReCl(CO)(dppm)$_2$], **1** showing the atom numbering scheme adopted for each of the two independent molecules; (b) The rhenium coordination in the ordered molecule of **1** showing 50% probability ellipsoids.

of analogous complexes [2a]. The low values of $\nu$(CO) indicate that the rhenium centres are electron rich, and that back-bonding to the carbonyl ligands is strong [8]. In addition, the IR spectrum of **2** also shows two intense bands at 920 cm$^{-1}$ and 906 cm$^{-1}$ caused by $\nu$(ReO) vibrations of the perrhenate group. The observation of two $\nu$(ReO) stretching vibrations, rather than the single broad-band characteristic of free [ReO$_4$]$^-$ [9], is indicative of the coordination of the perrhenate group and consistent with the structure revealed by X-ray diffraction analysis.

Previous study has placed ReO$_4^-$ below Cl$^-$ in the spectrochemical series [10], and the weaker ligation of perrhenate compared to chloride is also indicated by the higher value of $\nu$(CO) for **2** than for **1**. Consistent with this conclusion is the observation that addition of NaCl to a solution of [Re(OReO$_3$)(CO)(dppm)$_2$], **2**, readily leads to displacement of ReO$_4^-$ by Cl$^-$, with formation of **1**.

The perrhenate complex **2** is of special interest because it contains rhenium atoms in two such different oxidation states. Although a limited body of work has demonstrated that ReO$_4^-$ can act as a ligand [1,10], it is rarely found in complexes that contain metals in low oxidation states and that have organometallic functionality. In fact, we are aware of no perrhenate complex of rhenium(I). Examples of perrhenate groups bound to rhenium are found in rhenium(V) compounds

such as [ReOI$_2$(OReO$_3$)(PPh$_3$)$_2$] [4] and [Re$_2$O($\mu$-O)$_2$(C$_5$Me$_5$)$_2$(OReO$_3$)$_2$] [5]. It is therefore noteworthy that rhenium(I) and rhenium(VII) can coexist in complex **2**, and that the complex appears to be inert towards intramolecular redox reactivity. The perrhenate complex **2** may also be considered as a binuclear complex with Re$^I$ and Re$^{VII}$ centres bridged by an oxo ligand. Bimetallic complexes such as this are novel because of the large disparity in metal oxidation states and the difference in coordination environments of the two metal centres. For example, the complex [Re$_2$($\mu$-O)(O)Cl$_4$($\mu$-dppm)$_2$(CN-2,6-xylyl)] is considered to contain a Cl-Re$^{III}$ $\cdots$ O=Re$^V$=O linkage, in which the oxidation states of the rhenium centres differ by only two units [11]. A closely related compound, [ReCl$_2$-ReO$_3$(dmpm)$_2$] (dmpm = Me$_2$PCH$_2$PMe$_2$), contains a ReO$_3$ unit that is metal–metal bonded to a ReCl$_2$(dmpm)$_2$ unit, and is therefore formally a Re$^{II}$–Re$^{VI}$ complex [12]. The complex **2** which is formulated as Re$^I$–Re$^{VII}$, completes a series in which the oxidation states of two adjacent rhenium atoms total eight, but are factored as III–V, II–VI or I–VII.

## 3. Experimental details

IR spectra were recorded with a Perkin-Elmer 2000 spectrometer, and the NMR spectra were recorded by using a Varian Gemini-300 with chemical shifts being referred to TMS ($^1$H) and 85% H$_3$PO$_4$ ($^{31}$P{$^1$H}).
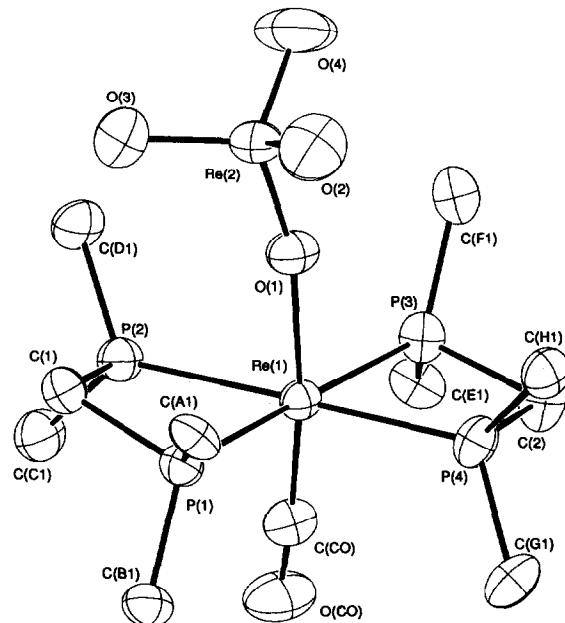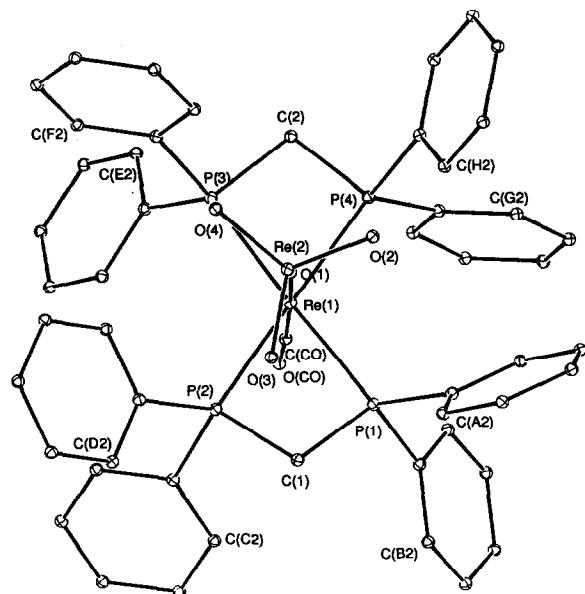


Fig. 2. (a) A view of a molecule of [Re(ReO$_4$(CO)(dppm)$_2$], **2** showing the atom numbering; (b) The coordination of the rhenium atoms in **2** showing 50% probability ellipsoids.

TABLE 1. Selected bond lengths (Å) and angles (°) in [ReCl(CO)(dppm)₂], 1

| | | | |
|---|---|---|---|
| Re(1)–Cl(1) | 2.543(2) | Re(1)–P(11) | 2.395(2) |
| Re(1)–P(12) | 2.396(2) | Re(1)–P(13) | 2.394(2) |
| Re(1)–P(14) | 2.384(3) | Re(1)–C(1) | 1.869(9) |
| Re(2)–Cl(X) | 2.565(5) | Re(2)–Cl(Y) | 2.606(9) |
| Re(2)–P(21) | 2.404(3) | Re(2)–P(22) | 2.375(2) |
| Re(2)–P(23) | 2.395(2) | Re(2)–P(24) | 2.400(3) |
| Re(2)–C(X) | 1.914(17) | Re(2)–C(Y) | 1.95(3) |
| P(11)–C(11) | 1.840(8) | P(12)–C(11) | 1.849(8) |
| P(13)–C(12) | 1.852(9) | P(14)–C(12) | 1.854(8) |
| P(21)–C(21) | 1.859(8) | P(22)–C(21) | 1.854(9) |
| P(23)–C(22) | 1.855(8) | P(24)–C(22) | 1.855(8) |
| O(X)–C(X) | 1.07(3) | O(Y)–C(Y) | 1.00(4) |
| O(1)–C(1) | 1.133(11) | | |

| | | | |
|---|---|---|---|
| Cl(1)–Re(1)–P(11) | 89.8(1) | Cl(1)–Re(1)–P(12) | 86.6(1) |
| Cl(1)–Re(1)–P(13) | 87.4(1) | Cl(1)–Re(1)–P(14) | 90.6(1) |
| Cl(1)–Re(1)–C(1) | 179.7(3) | P(11)–Re(1)–P(12) | 69.7(1) |
| P(11)–Re(1)–P(13) | 109.6(1) | P(11)–Re(1)–P(14) | 179.5(1) |
| P(11)–Re(1)–C(1) | 90.3(3) | P(12)–Re(1)–P(13) | 174.0(1) |
| P(12)–Re(1)–P(14) | 110.5(1) | P(12)–Re(1)–C(1) | 93.3(3) |
| P(13)–Re(1)–P(14) | 70.3(1) | P(13)–Re(1)–C(1) | 92.3(3) |
| P(14)–Re(1)–C(1) | 89.2(3) | Cl(X)–Re(2)–P(21) | 99.0(2) |
| Cl(X)–Re(2)–P(22) | 97.3(2) | Cl(X)–Re(2)–P(23) | 81.4(2) |
| Cl(X)–Re(2)–P(24) | 82.4(2) | Cl(X)–Re(2)–C(X) | 177.2(5) |
| P(21)–Re(2)–P(22) | 69.9(1) | P(21)–Re(2)–P(23) | 110.6(1) |
| P(21)–Re(2)–P(24) | 178.6(1) | P(21)–Re(2)–C(X) | 83.8(5) |
| P(22)–Re(2)–P(23) | 178.7(1) | P(22)–Re(2)–P(24) | 110.0(1) |
| P(22)–Re(2)–C(X) | 84.1(5) | P(23)–Re(2)–P(24) | 69.6(1) |
| P(23)–Re(2)–C(X) | 97.1(5) | P(24)–Re(2)–C(X) | 94.9(5) |
| Re(1)–P(11)–C(11) | 95.6(3) | Re(1)–P(12)–C(11) | 95.3(3) |
| Re(1)–P(13)–C(12) | 95.1(3) | Re(1)–P(14)–C(12) | 95.4(3) |
| Re(2)–P(21)–C(21) | 95.3(3) | Re(2)–P(22)–C(21) | 96.5(3) |
| Re(2)–P(23)–C(22) | 95.5(3) | Re(2)–P(24)–C(22) | 95.4(3) |
| Re(2)–C(X)–O(X) | 175.5(15) | Re(1)–C(1)–O(1) | 177.7(7) |
| P(11)–C(11)–P(12) | 95.8(4) | P(13)–C(12)–P(14) | 95.9(4) |
| P(21)–C(21)–P(22) | 95.0(4) | P(23)–C(22)–P(24) | 95.1(4) |

Note: the Cl and CO ligands attached to Re(2) are disordered over two trans sites; sites labelled X have an occupancy of 0.61(1) and those labelled Y an occupancy of 0.39(1).

### 3.1. [ReCl(CO)(dppm)₂], 1

In a typical experiment, CO was bubbled for about 10 min through a suspension of Re₂Cl₁₀ (73 mg, 0.20 mmol) and dppm (77 mg, 0.20 mmol) in EtOH (10 mL) and NaBH₄ (46 mg, 1.21 mmol) was then added. The mixture was stirred overnight, during which a yellow solid separated. The solvent was decanted and the product, compound 1, was washed with EtOH. Yield 50%. ¹H NMR (CD₂CL₂): 5.75 (m, 2H, CH₂P₂); 5.56 (m, 2H, CH₂P₂) ppm. ³¹P NMR: −29 (s, dppm) ppm. IR (Nujol): ν(CO) 1848, 1831 cm⁻¹.

### 3.2. [Re(ReO₄)(CO)(dppm)₂], 2

Compound 2 was prepared in a manner similar to that described for 1. Thus CO was bubbled for about 10 min through a suspension of NH₄ReO₄ (108 mg, 0.40 mmol) and dppm (158 mg, 0.41 mmol) in EtOH

TABLE 2. Selected bond lengths (Å) and angles (°) in [Re(OReO₃)(CO)(dppm)₂], 2

| | | | |
|---|---|---|---|
| Re(1)–P(1) | 2.401(2) | Re(1)–P(2) | 2.399(2) |
| Re(1)–P(3) | 2.380(2) | Re(1)–P(4) | 2.382(2) |
| Re(1)–O(1) | 2.207(3) | Re(1)–C(CO) | 1.857(5) |
| Re(2)–O(1) | 1.754(3) | Re(2)–O(2) | 1.701(4) |
| Re(2)–O(3) | 1.703(4) | Re(2)–O(4) | 1.695(5) |
| P(1)–C(1) | 1.849(5) | P(2)–C(1) | 1.854(5) |
| P(3)–C(2) | 1.863(5) | P(4)–C(2) | 1.837(6) |
| O(CO)–C(CO) | 1.175(7) | | |

| | | | |
|---|---|---|---|
| P(1)–Re(1)–P(2) | 69.8(1) | P(1)–Re(1)–P(3) | 178.2(1) |
| P(1)–Re(1)–P(4) | 108.0(1) | P(1)–Re(1)–O(1) | 84.1(1) |
| P(1)–Re(1)–C(CO) | 92.8(2) | P(2)–Re(1)–P(3) | 111.9(1) |
| P(2)–Re(1)–P(4) | 177.7(1) | P(2)–Re(1)–O(1) | 84.5(1) |
| P(2)–Re(1)–C(CO) | 89.0(2) | P(3)–Re(1)–P(4) | 70.3(1) |
| P(3)–Re(1)–O(1) | 95.6(1) | P(3)–Re(1)–C(CO) | 87.7(2) |
| P(4)–Re(1)–O(1) | 94.5(1) | P(4)–Re(1)–C(CO) | 92.0(2) |
| O(1)–Re(1)–C(CO) | 173.4(2) | O(1)–Re(2)–O(2) | 109.6(2) |
| O(1)–Re(2)–O(3) | 110.2(2) | O(1)–Re(2)–O(4) | 110.2(2) |
| O(2)–Re(2)–O(3) | 108.7(2) | O(2)–Re(2)–O(4) | 109.0(3) |
| O(3)–Re(2)–O(4) | 109.0(3) | Re(1)–P(1)–C(1) | 95.3(2) |
| Re(1)–P(2)–C(1) | 95.2(2) | Re(1)–P(3)–C(2) | 96.2(2) |
| Re(1)–P(4)–C(2) | 96.8(2) | Re(1)–O(1)–Re(2) | 167.1(2) |
| Re(1)–C(CO)–O(CO) | 176.5(5) | P(1)–C(1)–P(2) | 95.8(3) |
| P(3)–C(2)–P(4) | 95.6(3) | | |

(15 mL), and NaBH₄ (65 mg, 1.71 mmol) in EtOH (3 mL) was then added. There was an immediate colour change to yellow. The mixture was stirred overnight, during which a yellow solid separated. The solvent was decanted and the product [Re(OReO₃)(CO)(dppm)₂] was washed with EtOH. Yield 40%. ¹H NMR (CD₂Cl₂): 5.79 (m, 2H, CH₂P₂); 5.54 (m, 2H, CH₂P₂); ³¹P NMR: −21 (s, dppm) ppm. IR (Nujol): ν(CO) 1862 cm⁻¹.

### 3.3. X-ray analysis of [ReCl(CO)(dppm)₂], 1, and [Re(ReO₄)(CO)(dppm)₂], 2

The X-ray measurements were made at ambient temperature, with graphite monochromated molybdenum radiation and an Enraf-Nonius CAD4 diffractometer. Crystals of both compounds were orange-yellow plates grown from C₂H₂Cl₂/diethyl ether solutions.

The unit cell dimensions (Table 4) were determined by a least-squares treatment of diffractometric angles for 25 Bragg reflections, with $17.6 \le \Theta \le 20.5°$ for 1

TABLE 3. IR and NMR data for compounds 1 and 2

| Complex | IR (cm⁻¹) [a] | ¹H [b] NMR | ³¹P NMR |
|---|---|---|---|
| 1 | 1848 (st) | 5.75 (m) | −29 (s) |
| | 1831 (st) | 5.56 (m) | |
| 2 | 1862 (st) | 5.79 (m) | −21 (s) |
| | | 5.54 (m) | |

[a] Nujol mulls, ν(CO), st = strong. [b] CH₂P₂, in CD₂Cl₂, s = singlet.

TABLE 4. Crystallographic data for the complexes *trans*-[ReCl(CO)(dppm)₂] 1 and *trans*-[Re(ReO₄)(CO)(dppm)₂] 2

| Compound | 1 | 2 |
|---|---|---|
| Formula | $C_{51}H_{44}ClOP_4Re$ | $C_{51}H_{44}O_5P_4Re_2$ |
| Formula weight | 1018.5 | 1233.2 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/c$ | $P2_1/n$ |
| $a$, Å | 15.394(1) | 13.596(2) |
| $b$, Å | 19.385(4) | 15.542(1) |
| $c$, Å | 29.385(14) | 22.942(1) |
| $\beta$, deg. | 92.27(2) | 102.001(6) |
| $U$, Å³ | 8762(5) | 4741.8(6) |
| $Z$ | 8 | 4 |
| $D_{calcd}$, g cm⁻³ | 1.544 | 1.727 |
| $\mu$(Mo–K$\alpha$), cm⁻¹ | 30.5 | 53.5 |
| Crystal size, mm | 0.44×0.45×0.25 | 0.28×0.18×0.18 |
| Absorption factors (on $F$) | 0.88–1.11 | 0.85–1.41 |
| Temperature, °C | 25 | 26 |
| $\theta$ range, deg. | 2.6–25.0 | 2.1–30.4 |
| $h$ | 0–18 | 0–19 |
| $k$ | $\overline{23}$–0 | 0–22 |
| $l$ | $\overline{35}$–35 | $\overline{32}$–32 |
| Unique reflections | 15365 | 14335 |
| Observed reflections | 10495 | 9141 |
| $R$ | 0.041 | 0.034 |
| $R_w$ | 0.049 | 0.035 |
| Parameters refined | 348 | 464 |
| Maximum $\Delta/\sigma$ | 0.10 | 0.36 |
| Maximum $|\Delta\rho|$, e/Å³ | 1.1 | 1.4 |

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w^{-1/2} = \sigma(F_o)$. Mo–K$\alpha$ X-radiation, $\lambda = 0.71069$ Å, was used for both experiments.

and $20.7 \le \Theta \le 22.8°$ for **2**. A primitive crystal lattice and the $2/m$ Laue symmetry were established for each compound by investigation of the diffraction pattern, and the space group symmetry was determined from the systematic absences.

The intensities of reflections were measured by $\omega/2\Theta$ scans of $(0.86 + 0.58 \tan \Theta)$ and $(0.48 + 0.58 \tan \Theta)°$ in $\Theta$ for **1** and **2** respectively, and the scan speeds were adjusted to give $\sigma(I)/I < 0.03$, subject to a time limit of 30 s. For both compounds three standard reflections measured every 2 h throughout data collection, showed no significant variations in intensity. The integrated intensities of all reflections, derived in the usual manner ($q = 0.03$) [13], were corrected for Lorentz, polarization and absorption effects. For **1** 15,977 intensities were measured; of the 15,365 unique reflections 10,495 for which $I \ge 3\sigma(I)$ were used; for **2** 14,876 reflections were measured; 14,325 were unique, and of these 9,141 with $I \ge 2\sigma(I)$ were used in the structure analysis.

For both compounds, the positions of non-hydrogen atoms were determined from Patterson and difference electron density functions. Hydrogen atoms were in-

TABLE 5. Fractional coordinates and isotropic displacement parameters (Å²) for [ReCl(CO)(dppm)₂] 1

| | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| Re(1) | 0.24963(2) | 0.19755(1) | −0.01248(1) | 0.024 |
| Re(2) | −0.24408(2) | 0.21611(2) | −0.26720(1) | 0.026 |
| CL(X) | −0.1830(3) | 0.0955(3) | −0.2497(2) | 0.046(1) |
| CL(Y) | −0.3105(5) | 0.3377(5) | −0.2836(3) | 0.046 |
| CL(1) | 0.25473(14) | 0.06710(10) | −0.00365(7) | 0.046 |
| P(11) | 0.17400(12) | 0.20626(9) | 0.05698(6) | 0.027 |
| P(12) | 0.09630(12) | 0.18459(10) | −0.02718(7) | 0.028 |
| P(13) | 0.40311(12) | 0.19786(10) | 0.00416(7) | 0.032 |
| P(14) | 0.32511(12) | 0.18985(10) | −0.08158(7) | 0.031 |
| P(21) | −0.24551(13) | 0.21178(11) | −0.34900(7) | 0.035 |
| P(22) | −0.38310(12) | 0.18085(110 | −0.29642(7) | 0.032 |
| P(23) | −0.10333(12) | 0.24913(10) | −0.23707(7) | 0.030 |
| P(24) | −0.24417(12) | 0.22316(10) | −0.18565(7) | 0.029 |
| O(X) | −0.3152(10) | 0.3581(9) | −0.2799(5) | 0.079(5) |
| O(Y) | −0.1810(14) | 0.0733(13) | −0.2606(8) | 0.079 |
| O(1) | 0.2417(4) | 0.3515(3) | −0.0227(2) | 0.054 |
| C(X) | −0.2887(9) | 0.3072(9) | −0.2771(5) | 0.040(3) |
| C(Y) | −0.1995(14) | 0.1226(13) | −0.2609(8) | 0.040 |
| C(1) | 0.2465(5) | 0.2934(4) | −0.0190(2) | 0.034 |
| C(11) | 0.0698(5) | 0.1732(4) | 0.0332(3) | 0.032(2) |
| C(12) | 0.4328(5) | 0.1714(4) | −0.0538(3) | 0.042(2) |
| C(21) | −0.3655(5) | 0.2038(4) | −0.3566(3) | 0.041(2) |
| C(22) | −0.1241(5) | 0.2254(4) | −0.1773(3) | 0.034(2) |
| C(111) | 0.1874(3) | 0.1608(4) | 0.1120(2) | 0.030(2) |
| C(112) | 0.1384(4) | 0.1808(3) | 0.1480(3) | 0.038(2) |
| C(113) | 0.1437(5) | 0.1443(2) | 0.1884(3) | 0.050(2) |
| C(114) | 0.1981(3) | 0.0878(3) | 0.1927(2) | 0.048(2) |
| C(115) | 0.2471(4) | 0.0679(3) | 0.1566(3) | 0.049(2) |
| C(116) | 0.2417(5) | 0.1043(2) | 0.1163(2) | 0.039(2) |
| C(121) | 0.1578(7) | 0.2957(2) | 0.0744(3) | 0.032(2) |
| C(122) | 0.0873(6) | 0.3349(5) | 0.0595(2) | 0.056(2) |
| C(123) | 0.0864(3) | 0.4050(5) | 0.0676(3) | 0.072(3) |
| C(124) | 0.1559(6) | 0.4360(2) | 0.0906(3) | 0.077(3) |
| C(125) | 0.2264(5) | 0.3969(5) | 0.1054(2) | 0.061(3) |
| C(126) | 0.2273(4) | 0.3268(5) | 0.0973(4) | 0.046(2) |
| C(131) | 0.0241(4) | 0.2549(4) | −0.0467(4) | 0.035(2) |
| C(132) | −0.0632(4) | 0.2495(3) | −0.0384(2) | 0.047(2) |
| C(133) | −0.1197(3) | 0.3013(3) | −0.0524(2) | 0.064(3) |
| C(134) | −0.0889(4) | 0.3583(4) | −0.0748(3) | 0.075(3) |
| C(135) | −0.0016(3) | 0.3636(2) | −0.0831(2) | 0.068(3) |
| C(136) | 0.0549(3) | 0.3119(4) | −0.0691(3) | 0.053(2) |
| C(141) | 0.0418(6) | 0.1146(5) | −0.0592(2) | 0.035(2) |
| C(142) | −0.0165(6) | 0.0695(4) | −0.0407(2) | 0.042(2) |
| C(143) | −0.0608(3) | 0.0226(2) | −0.0682(1) | 0.059(3) |
| C(144) | −0.0468(5) | 0.0207(4) | −0.1143(2) | 0.059(3) |
| C(145) | 0.0115(5) | 0.0658(3) | −0.1328(2) | 0.061(3) |
| C(146) | 0.0558(4) | 0.1127(3) | −0.1053(1) | 0.047(2) |
| C(151) | 0.4603(3) | 0.1400(5) | 0.0445(3) | 0.036(2) |
| C(152) | 0.4500(5) | 0.1536(3) | 0.0901(4) | 0.053(2) |
| C(153) | 0.4933(6) | 0.1142(3) | 0.1229(2) | 0.064(3) |
| C(154) | 0.5470(3) | 0.0612(4) | 0.1101(3) | 0.064(3) |
| C(155) | 0.5573(6) | 0.0475(3) | 0.0645(3) | 0.065(3) |
| C(156) | 0.5140(6) | 0.0869(4) | 0.0318(2) | 0.052(2) |
| C(161) | 0.4668(7) | 0.2774(4) | 0.0158(2) | 0.040(2) |
| C(162) | 0.5552(7) | 0.2763(2) | 0.0099(4) | 0.056(2) |
| C(163) | 0.6044(4) | 0.3346(4) | 0.0190(3) | 0.074(3) |
| C(164) | 0.5651(6) | 0.3939(4) | 0.0340(2) | 0.084(3) |
| C(165) | 0.4767(6) | 0.3950(3) | 0.0399(3) | 0.080(3) |
| C(166) | 0.4275(3) | 0.3367(5) | 0.0309(3) | 0.055(2) |
| C(171) | 0.3339(4) | 0.2718(3) | −0.1115(3) | 0.041(2) |

TABLE 5 (continued)

| | x | y | z | U |
|---|---|---|---|---|
| C(172) | 0.3989(4) | 0.3188(6) | −0.1008(3) | 0.060(3) |
| C(173) | 0.3974(5) | 0.3831(5) | −0.1209(2) | 0.073(3) |
| C(174) | 0.3309(4) | 0.4005(3) | −0.1517(3) | 0.072(3) |
| C(175) | 0.2659(4) | 0.3535(5) | −0.1623(3) | 0.068(3) |
| C(176) | 0.2673(6) | 0.2891(4) | −0.1422(2) | 0.050(2) |
| C(181) | 0.3177(7) | 0.1273(3) | −0.1292(2) | 0.032(2) |
| C(182) | 0.3649(5) | 0.1377(3) | −0.1675(2) | 0.043(2) |
| C(183) | 0.3620(3) | 0.0895(2) | −0.2022(2) | 0.049(2) |
| C(184) | 0.3118(5) | 0.0310(3) | −0.1985(2) | 0.050(2) |
| C(185) | 0.2645(3) | 0.0206(3) | −0.1601(1) | 0.049(2) |
| C(186) | 0.2675(5) | 0.0687(3) | −0.1255(2) | 0.038(2) |
| C(211) | −0.2059(8) | 0.1405(3) | −0.3847(3) | 0.037(2) |
| C(212) | −0.1692(5) | 0.1521(2) | −0.4262(3) | 0.055(2) |
| C(213) | −0.1482(4) | 0.0970(3) | −0.4534(2) | 0.073(3) |
| C(214) | −0.1638(6) | 0.0305(3) | −0.4392(3) | 0.069(3) |
| C(215) | −0.2005(4) | 0.0189(3) | −0.3978(2) | 0.081(3) |
| C(216) | −0.2215(6) | 0.0740(3) | −0.3706(2) | 0.074(3) |
| C(221) | −0.2130(4) | 0.2882(2) | −0.3821(2) | 0.042(2) |
| C(222) | −0.2660(5) | 0.3192(5) | −0.4150(2) | 0.058(2) |
| C(223) | −0.2375(4) | 0.3768(5) | −0.4377(3) | 0.070(3) |
| C(224) | −0.1559(3) | 0.4033(2) | −0.4274(2) | 0.062(3) |
| C(225) | −0.1028(4) | 0.3723(5) | −0.3945(2) | 0.059(3) |
| C(226) | −0.1313(3) | 0.3148(5) | −0.3718(3) | 0.050(2) |
| C(231) | −0.4215(5) | 0.0906(3) | −0.2948(2) | 0.043(2) |
| C(232) | −0.4853(3) | 0.0674(5) | −0.3253(3) | 0.067(3) |
| C(233) | −0.5268(5) | 0.0055(5) | −0.3177(2) | 0.084(3) |
| C(234) | −0.5045(4) | −0.0329(3) | −0.2795(2) | 0.070(3) |
| C(235) | −0.4406(4) | −0.0097(5) | −0.2490(3) | 0.070(3) |
| C(236) | −0.3991(6) | 0.0521(6) | −0.2566(2) | 0.047(2) |
| C(241) | −0.4840(5) | 0.2259(3) | −0.2829(3) | 0.038(2) |
| C(242) | −0.4876(4) | 0.2599(5) | −0.2417(3) | 0.040(2) |
| C(243) | −0.5633(6) | 0.2924(4) | −0.2301(2) | 0.052(2) |
| C(244) | −0.6353(4) | 0.2909(3) | −0.2595(3) | 0.058(3) |
| C(245) | −0.6317(4) | 0.2569(5) | −0.3007(2) | 0.067(3) |
| C(246) | −0.5560(6) | 0.2244(3) | −0.3123(3) | 0.053(2) |
| C(251) | −0.0032(5) | 0.2026(3) | −0.2509(4) | 0.035(2) |
| C(252) | 0.0015(4) | 0.1751(6) | −0.2940(3) | 0.046(2) |
| C(253) | 0.0764(6) | 0.1422(4) | −0.3066(2) | 0.063(3) |
| C(254) | 0.1464(4) | 0.1368(3) | −0.2761(3) | 0.067(3) |
| C(255) | 0.1417(4) | 0.1643(5) | −0.2329(2) | 0.069(3) |
| C(256) | 0.0669(7) | 0.1972(4) | −0.2203(3) | 0.056(2) |
| C(261) | −0.0643(5) | 0.3394(3) | −0.2344(2) | 0.035(2) |
| C(262) | −0.0984(6) | 0.3856(5) | −0.2661(2) | 0.044(2) |
| C(263) | −0.687(3) | 0.4527(4) | −0.2666(3) | 0.057(3) |
| C(264) | −0.0048(5) | 0.4737(3) | −0.2353(2) | 0.064(3) |
| C(265) | 0.0294(5) | 0.4276(5) | −0.2037(2) | 0.062(3) |
| C(266) | −0.0004(3) | 0.3605(4) | −0.2032(2) | 0.052(2) |
| C(271) | −0.2807(6) | 0.3024(2) | −0.1571(3) | 0.033(2) |
| C(272) | −0.2499(5) | 0.3647(2) | −0.1727(2) | 0.042(2) |
| C(273) | −0.2689(3) | 0.4250(2) | −0.1502(2) | 0.047(2) |
| C(274) | −0.3187(5) | 0.4231(2) | −0.1122(3) | 0.050(2) |
| C(275) | −0.3496(4) | 0.3609(2) | −0.0967(2) | 0.053(2) |
| C(276) | −0.3305(4) | 0.3006(2) | −0.1191(2) | 0.048(2) |
| C(281) | −0.2843(3) | 0.1569(2) | −0.1469(2) | 0.038(2) |
| C(282) | −0.2359(4) | 0.1336(4) | −0.1095(2) | 0.047(2) |
| C(283) | −0.2714(4) | 0.0870(5) | −0.0800(2) | 0.055(2) |
| C(284) | −0.3554(2) | 0.0638(2) | −0.0879(2) | 0.055(2) |
| C(285) | −0.4038(4) | 0.0871(4) | −0.1253(2) | 0.049(2) |
| C(286) | −0.3683(4) | 0.1337(5) | −0.1549(3) | 0.044(2) |

Note: both here and in Table 6: $U = \frac{1}{3}\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i^*a_j^*(\vec{a}_i.\vec{a}_j)$.

TABLE 6. Fractional coordinates and isotropic displacement parameters (Å²) for [Re(OReO₃)(CO)(dppm)₂] 2

| | x | y | z | U |
|---|---|---|---|---|
| Re(1) | 0.85797(1) | 0.25772(1) | 0.10471(1) | 0.029 |
| Re(2) | 0.66160(2) | 0.13700(1) | 0.17945(1) | 0.043 |
| P(1) | 0.75969(9) | 0.37774(7) | 0.12571(5) | 0.033 |
| P(2) | 0.91292(9) | 0.30214(8) | 0.20645(5) | 0.036 |
| P(3) | 0.95169(9) | 0.13801(8) | 0.08110(5) | 0.037 |
| P(4) | 0.79709(9) | 0.21649(9) | 0.00364(5) | 0.038 |
| O(1) | 0.7465(2) | 0.1805(2) | 0.1394(1) | 0.040 |
| O(2) | 0.5437(3) | 0.1376(3) | 0.1362(2) | 0.072 |
| O(3) | 0.6614(3) | 0.1966(3) | 0.2417(2) | 0.068 |
| O(4) | 0.6941(4) | 0.0344(3) | 0.1999(2) | 0.093 |
| O(CO) | 1.0203(3) | 0.3727(3) | 0.0743(2) | 0.067 |
| C(CO) | 0.9557(3) | 0.3283(3) | 0.0842(2) | 0.041 |
| C(1) | 0.8022(3) | 0.3713(3) | 0.2076(2) | 0.038 |
| C(2) | 0.8952(4) | 0.1366(3) | −0.0002(2) | 0.051 |
| C(A1) | 0.6208(2) | 0.3793(4) | 0.1102(2) | 0.039 |
| C(A2) | 0.5668(3) | 0.3631(4) | 0.1537(2) | 0.047 |
| C(A3) | 0.4631(3) | 0.3622(2) | 0.1394(1) | 0.068 |
| C(A4) | 0.4133(2) | 0.3774(3) | 0.0815(2) | 0.069 |
| C(A5) | 0.4673(3) | 0.3936(3) | 0.0379(2) | 0.063 |
| C(A6) | 0.5710(3) | 0.3946(2) | 0.0523(2) | 0.052 |
| C(B1) | 0.7903(3) | 0.4852(2) | 0.1013(2) | 0.039 |
| C(B2) | 0.7863(3) | 0.5573(2) | 0.1359(1) | 0.051 |
| C(B3) | 0.8050(4) | 0.6375(2) | 0.1147(2) | 0.065 |
| C(B4) | 0.8277(3) | 0.6456(2) | 0.0591(2) | 0.066 |
| C(B5) | 0.8316(3) | 0.5735(2) | 0.0246(2) | 0.061 |
| C(B6) | 0.8129(5) | 0.4933(2) | 0.0457(2) | 0.049 |
| C(C1) | 1.0234(5) | 0.3708(5) | 0.2331(1) | 0.049 |
| C(C2) | 1.0176(3) | 0.4594(5) | 0.2298(3) | 0.066 |
| C(C3) | 1.1018(4) | 0.5087(3) | 0.2513(3) | 0.094 |
| C(C4) | 1.1918(4) | 0.4693(4) | 0.2761(1) | 0.099 |
| C(C5) | 1.1976(3) | 0.3808(4) | 0.2794(3) | 0.092 |
| C(C6) | 1.1134(5) | 0.3315(2) | 0.2579(3) | 0.070 |
| C(D1) | 0.9222(2) | 0.2265(3) | 0.2681(2) | 0.042 |
| C(D2) | 0.9238(4) | 0.2536(2) | 0.3255(2) | 0.055 |
| C(D3) | 0.9362(5) | 0.1944(3) | 0.3713(2) | 0.067 |
| C(D4) | 0.9469(2) | 0.1082(3) | 0.3597(2) | 0.076 |
| C(D5) | 0.9453(4) | 0.0812(2) | 0.3022(2) | 0.069 |
| C(D6) | 0.9329(5) | 0.1403(3) | 0.2564(2) | 0.053 |
| C(E1) | 1.0871(2) | 0.1465(4) | 0.0865(3) | 0.042 |
| C(E2) | 1.1348(5) | 0.1139(5) | 0.0438(1) | 0.060 |
| C(E3) | 1.2378(4) | 0.1212(2) | 0.0509(3) | 0.085 |
| C(E4) | 1.2931(2) | 0.1612(4) | 0.1009(2) | 0.085 |
| C(E5) | 1.2453(5) | 0.1938(4) | 0.1436(2) | 0.085 |
| C(E6) | 1.1424(4) | 0.1864(2) | 0.1365(3) | 0.068 |
| C(F1) | 0.9352(4) | 0.0277(2) | 0.1071(2) | 0.046 |
| C(F2) | 1.0156(4) | −0.0201(4) | 0.1370(2) | 0.083 |
| C(F3) | 0.9991(3) | −0.0991(4) | 0.1608(3) | 0.112 |
| C(F4) | 0.9025(3) | −0.1302(2) | 0.1547(2) | 0.095 |
| C(F5) | 0.8222(4) | −0.0824(4) | 0.1248(3) | 0.091 |
| C(F6) | 0.8386(3) | −0.0034(4) | 0.1010(3) | 0.066 |
| C(G1) | 0.8001(3) | 0.2958(3) | −0.0558(2) | 0.049 |
| C(G2) | 0.7113(3) | 0.3316(4) | −0.0862(2) | 0.073 |
| C(G3) | 0.7133(3) | 0.4022(5) | −0.1225(3) | 0.109 |
| C(G4) | 0.8042(3) | 0.4371(3) | −0.1282(2) | 0.107 |
| C(G5) | 0.8930(3) | 0.4013(4) | −0.0978(2) | 0.101 |
| C(G6) | 0.8910(3) | 0.3307(5) | −0.0616(3) | 0.071 |
| C(H1) | 0.6777(4) | 0.1591(4) | −0.0219(1) | 0.042 |
| C(H2) | 0.5999(5) | 0.1731(3) | 0.0071(2) | 0.045 |
| C(H3) | 0.5092(3) | 0.1313(2) | −0.0115(2) | 0.062 |
| C(H4) | 0.4964(3) | 0.0755(3) | −0.0593(1) | 0.068 |
| C(H5) | 0.5742(5) | 0.0614(3) | −0.0883(2) | 0.072 |
| C(H6) | 0.6648(3) | 0.1032(3) | −0.0697(2) | 0.060 |

cluded in the structural models in calculated positions (C–H = 0.96 Å), each with $U_{iso}$ fixed at about 1.2 $U_{eq}$ of the parent carbon atom. The methylenic hydrogens were allowed to ride on their parent carbon atoms. The phenyl groups were refined as rigid bodies, constrained to D$_{6h}$ symmetry with C–C = 1.38 Å and C–H = 0.96 Å. The structures were refined by least-squares minimization of the function $\Sigma w(|F_0| - |F_c|)^2$ with $w = [\sigma(|F_0|)]^{-2}$, using a large-block approximation to the normal matrix.

In crystals of **1**, one of the two independent molecules displays a disorder of the Cl and CO ligands over two sites on opposite sides of the ReP$_4$ plane such that the overall structure is the sum of $\alpha$[trans-Cl(X)–Re–C(X)O(X)] + (1 − $\alpha$)[trans-O(Y)C(Y)–Re–Cl(Y)], where the final value of the occupancy factor $\alpha$ = 0.61(1). Isotropic displacement parameters were refined for the disordered Cl, C and O atoms with the constraint that a single U$_{iso}$ parameter was used for each of the atom pairs [Cl(X), Cl(Y)], [C(X), C(Y)] and [O(X), O(Y)]. Anisotropic displacement parameters were used for all Re and P atoms and for Cl, C(CO) and O(CO) atoms of the ordered molecule. Adjustment of 348 parameters converged at $R = 0.041$ and $R$w = 0.049. For **2**, refinement of 464 parameters, including anisotropic displacement parameters for all non-hydrogen atoms converged at $R = 0.034$ and $R$w = 0.035.

Final atomic parameters for **1** and **2** are shown in Tables 5 and 6. The calculations were performed with the GX program system [15]. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref. 16.

Lists of atomic parameters and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre. Structure factor listings can be obtained from the authors.

## Acknowledgments

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