

THE STRUCTURE OF $[\text{Pt}_3(\text{ReO}_3)(\mu\text{-dppm})_3][\text{ReO}_4]_2$

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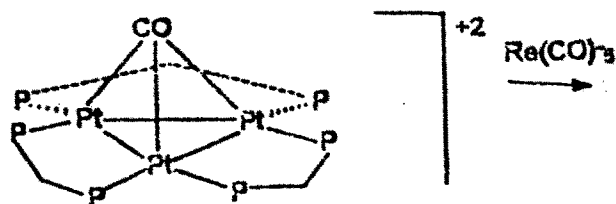
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Abstract

A cluster $[\text{Pt}_3(\text{ReO}_3)(\mu\text{-dppm})_3][\text{ReO}_4]_2$ with oxidation of $[\text{Pt}_3\text{Re}(\text{CO})_3(\mu\text{-dppm})_3][\text{PF}_6]$ is prepared. Crystals are triclinic, $P\bar{1}$; $a = 14.154(4)\text{\AA}$, $b = 14.213(3)\text{\AA}$, $c = 20.522(4)\text{\AA}$, $\alpha = 78.938(14)^\circ$, $\beta = 75.812(19)^\circ$, $\gamma = 74.957(22)^\circ$; $V = 3828.9(15)\text{\AA}^3$, $Z = 2$; Enraf-Nonius CAD4 diffractometer with $\text{Mo-K}\alpha$ radiation, $\lambda = 0.71073\text{\AA}$; $R = 0.069$, $R_w = 0.077$ for 284 parameters and 5414 reflections with $I \geq 3\sigma(I)$.

Introduction

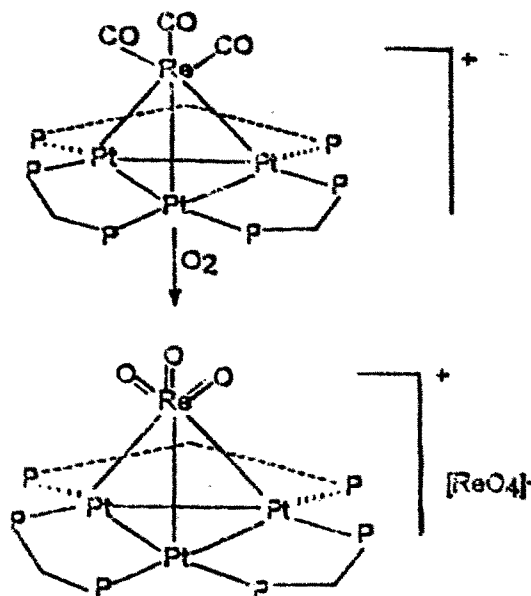
The cluster cation $[\text{Pt}_3(\mu\text{-ReO}_3)(\mu\text{-dppm})_3]^+$ in 2 contains both a high oxidation state $\text{Re(VII)}\text{O}_3^+$ fragment and a low oxidation state $\text{Pt}^0(\mu\text{-dppm})_3$ unit. The compound is formed by reaction of dioxygen with $[\text{Pt}_3\text{Re}(\text{CO})_3(\mu\text{-dppm})_3]^+$, 1, under forcing conditions. Complex 1 [15] can be obtained by reacting the parent



cluster $[\text{Pt}_3(\mu\text{-CO})(\mu\text{-dppm})_3]^{+2}$ with $[\text{Re}(\text{CO})_3]^-$ (Scheme 1).

The structure of 2 has been determined by X-ray diffraction and the results are presented in Table 1 and

Figures 1-3. The crystals contain $[\text{Pt}_3(\text{ReO}_3)(\mu\text{-dppm})_3]^+$ cluster cations based on a tetrahedral Pt_3Re core and $[\text{ReO}_4]^-$ anions.



Scheme 1. Reaction with dioxygen

Keywords: Characterisation; Cluster; Oxidation; Preparation; Structural model

Table 1. Selected bond distances (Å) and bond angles(°)

(a) bond distances					
Pt(1)-Pt(2)	2.598(2)	Pt(1)-Pt(3)	2.609(3)	Pt(2)-Pt(3)	2.600(3)
Pt(1)-Re(1)	2.720(3)	Pt(2)-Re(1)	2.748(3)	Pt(3)-Re(1)	2.711(3)
Re(1)-O(1)	1.74(3)	Re(1)-O(2)	1.70(3)	Re(1)-O(3)	1.77(3)
Re(2)-O(4)	1.71(4)	Re(2)-O(5)	1.80(4)	Re(2)-O(6)	1.67(3)
Re(2)-O(7)	1.68(4)				
(b) bond angles					
Pt(2)-Pt(1)-Pt(3)	59.9(1)	Pt(1)-Pt(3)-Pt(2)	59.8(1)		
Pt(1)-Pt(2)-Pt(3)	60.2(1)	Pt(2)-Pt(1)-Re(1)	62.2(1)		
Pt(3)-Pt(1)-Re(1)	61.1(1)	Pt(3)-Pt(2)-Re(1)	60.9(1)		
Pt(2)-Pt(3)-Re(1)	62.3(1)	Pt(1)-Re(1)-Pt(2)	56.7(1)		
Pt(1)-Pt(2)-Re(1)	61.1(1)	Pt(1)-Pt(3)-Re(1)	61.5(1)		
Pt(1)-Re(1)-Pt(3)	57.4(1)	Pt(2)-Re(1)-Pt(3)	56.9(1)		
Pt(1)-Re(1)-O(1)	88.8(8)	Pt(1)-Re(1)-O(2)	146.7(9)		
Pt(1)-Re(1)-O(3)	95.2(8)	Pt(2)-Re(1)-O(2)	95.7(9)		
Pt(2)-Re(1)-O(1)	142.7(8)	Pt(3)-Re(1)-O(1)	94.1(9)		
Pt(2)-Re(1)-O(3)	90.8(8)	Pt(3)-Re(1)-O(3)	145.0(8)		
Pt(3)-Re(1)-O(2)	92.9(9)	O(1)-Re(1)-O(3)	107.7(12)		
O(1)-Re(1)-O(2)	109.9(12)	O(4)-Re(2)-O(5)	103.5(17)		
O(2)-Re(1)-O(3)	104.4(12)	O(4)-Re(2)-O(7)	107.6(17)		
O(4)-Re(2)-O(6)	111.4(16)	O(5)-Re(2)-O(7)	110.7(17)		
O(5)-Re(2)-O(6)	113.5(16)	O(6)-Re(2)-O(7)	109.8(15)		

Results and Discussion

Each Pt-Pt edge is bridged by a dppm ligand, forming the well known latitudinal $Pt_3(\mu\text{-dppm})_3$ moiety. A face of the Pt_3 triangle is μ_3 -bridged by the $Re(1)O_3$ unit. Re(1) thereby adopts a highly distorted octahedral coordination which retains local C_3 symmetry, with Pt-Re(1)-Pt angles of $56.7(1)$ - $57.4(1)^\circ$ and O-Re-O angles of $104(1)$ - $110(1)^\circ$ (see Table 1). Thus, the cation in **2** is closely related structurally to $[Pt_3Re(CO)_3(\mu\text{-dppm})_3]^+$, **1**, with oxo ligands replacing carbonyl.

Each Pt_2P_2C ring adopts a distorted envelope conformation with a CH_2 group at the flap position. Two of the methylene carbon atoms lie on the same side of the Pt_3 triangle as Re(1) and the third methylene carbon [C(2)] is displaced to the other side of the Pt_3 triangle. The conformation of the $Pt_3P_2C_3$ unit brings two axial and four equatorial phenyl substituents to the side of the two CH_2 groups, affording a cavity which is occupied by the ReO_3 group. The cavity on the other side of the $Pt_3(\mu\text{-dppm})_3$ fragment, defined by four axial (A, D, I, L) and two equatorial (F, G) phenyl substituents, encloses a loosely bound $[ReO_4]^-$ anion (Fig. 1). The ability of the $M_3(\mu\text{-dppm})_3$ fragment in related complexes to attach and loosely bind an anion to one face of the M_3 triangle has been observed previously [6, 12]. Thus, for example, the short Pd-O distances [$2.77(1)$ - $2.92(2)$ Å] involving the $\mu\text{-CF}_3CO_2^-$ anion in $[Pd_3(\mu_3\text{-CO})_3(\mu\text{-CF}_3CO_2)(\mu\text{-dppm})_3]$

$[CF_3CO_2]^-$ [6] are considered indicative of some degree of covalency. In **2**, however, the shortest Pt-O distances [$3.37(3)$, $3.41(3)$, $3.98(3)$ Å] (Table 1) are too long to indicate a covalent bonding interaction.

The Pt-Pt distances in **1** are nearly constant [$2.593(1)$ - $2.611(1)$ Å], [15] and virtually identical values are found in **2** [$2.598(2)$ - $2.609(3)$ Å] (Table 1). The Pt-Re distances in each cluster are rather less regular, the values in **2** (Table 1) are slightly longer than those found in the parent compound **1** [15]. The Re(1)-O distances in **2** are in the range of $1.70(3)$ - $1.77(3)$ Å (Table 1) and compare well with corresponding values in the compounds $[C_9H_{10}N_6BReO_3]$ [$1.707(2)$ - $1.720(2)$ Å], [4], $[C_{10}H_{18}NReO_3]$ [$1.678(5)$ - $1.705(4)$ Å] [8], $[ReO_2(O_2C_6H_4)_2]$ [$1.681(7)$ Å] [5] and $[Re_2O_6(\mu_2\text{-OH})_2C_4H_8O_2]$ [$1.694(6)$ - $1.720(5)$ Å], [7]. The O-Re(1)-O angles in **2** [$104.4(12)$ - $109.9(12)^\circ$] lie between the values found in the compound $C_9H_{10}N_6BReO_3$ [$103.9(1)$ - $104.3(1)^\circ$] and those in $C_{10}H_{18}NReO_3$ [$119.1(3)$ - $119.5(1)^\circ$]. Bond distances and angles in the perrhenate anion are normal and agree with previous studies [13].

Each cation in **2** has closely associated with it an $[ReO_4]^-$ anion which blocks the free face of the Pt_3 triangle: the Re(2) atom is nearly equidistant from Pt(2) and Pt(3) [$4.97(8)$ & $4.96(2)$ Å respectively] and is slightly further [$5.29(2)$ Å] from Pt(1). The anion is

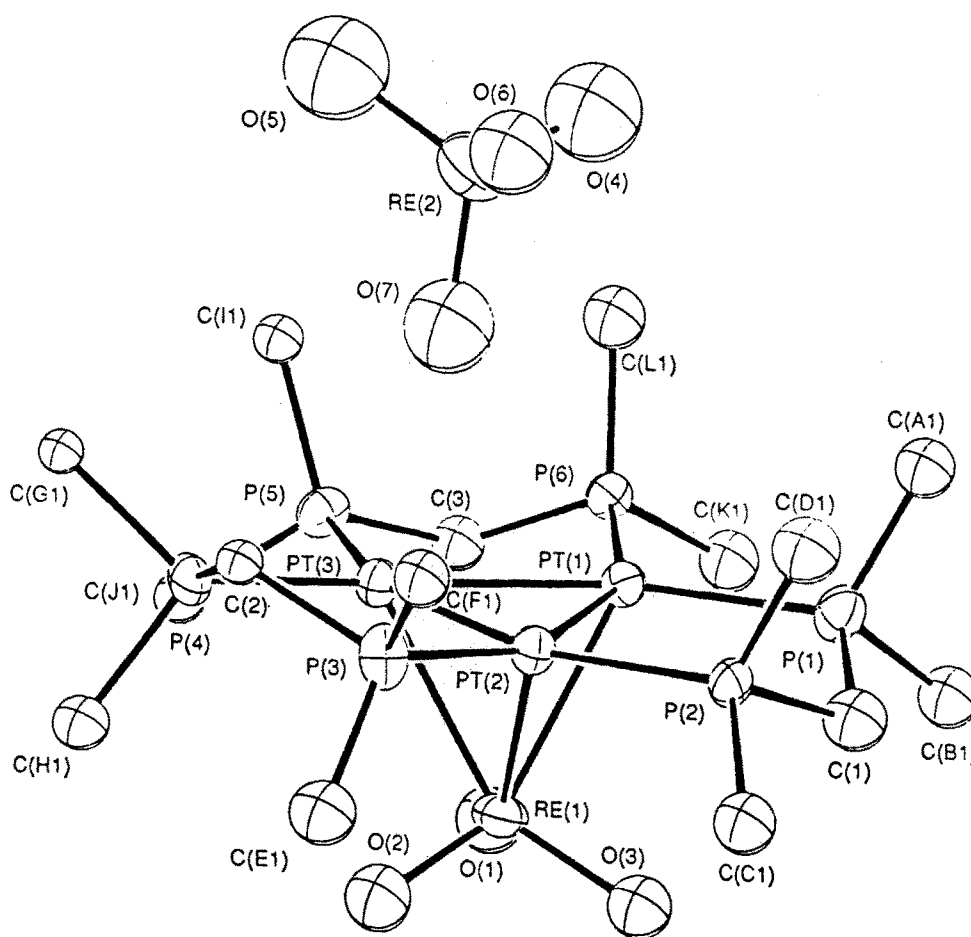


Figure 1. A view of the $[\text{Pt}_5(\text{ReO}_3)(\mu\text{-dppm})_3]^+$ cation in **2** and its associated $[\text{ReO}_3]^-$ anion. 50% probability ellipsoids are displayed. For clarity hydrogen atoms are omitted, as are all but the *ipso* carbon atoms of each of the twelve phenyl rings.

oriented so that the Re(2)-O(7) vector points towards the midpoint of Pt(2)-Pt(3). The resulting short O(7)... Pt contacts, as mentioned before, are however clearly nonbonding.

The overall transformation of **1** to **2** involves the replacement of the three carbonyl ligands in **1** by the three terminal oxo ligands in **2**. Since both CO and the terminal oxo ligand are formally two-electron donors, the overall cluster count in **1** and **2** are the same. Both are coordinatively unsaturated 54-electron clusters and the similarity displayed by the cluster cores of the two cations is therefore to be expected.

The bonding in both **2** and **1** can be understood in terms of the donation of electron density from three filled Pt-Pt bonding orbitals, having a a_1+e symmetry, of the $\text{Pt}_5(\mu\text{-dppm})_3$ fragment to the three vacant acceptor orbitals, also having a a_1+e symmetry, of an $\text{Re}(=\text{O})_3^+$ or $\text{Re}(\text{CO})_3$ fragment. In this formulation, the platinum and

rhenium atoms in **2** may be considered as Pt(0) and Re(VII). Even though this is an extreme interpretation, the oxidation states of platinum and rhenium in **2** are clearly very different, to an extent which is unprecedented in transition metal cluster chemistry.

The ReO_3 fragment is present in several other unusual compounds, such as MeReO_3 , $[(\eta^5\text{-C}_5\text{Me}_5)\text{ReO}_3]$ and $[\text{Me}_2\text{PCH}_2\text{PMe}_2)_2\text{Cl}_2\text{Re-ReO}_3]$. The first two of these are considered as Re(VII) complexes [2]. There is a useful analogy between complexes **2** and $[(\eta^5\text{-C}_5\text{Me}_5)\text{ReO}_3]$, since the donor orbitals of both the $\text{Pt}_5(\mu\text{-dppm})_3$ fragment and C_5Me_5 -ligand have a a_1+e symmetry and so may be considered to be isolobal [1]. The analogy, together with proven compatibility between the ReO_3^+ and $\text{Pt}_5(\mu\text{-dppm})_3$ fragments, suggests several other possibilities for preparing clusters, by substitution of $\text{Pt}_5(\mu\text{-dppm})_3$ units for C_5Me_5 -ligands derived from known $(\text{C}_5\text{Me}_5)\text{MX}_n$ complexes. Since the vast majority of organometallic oxo

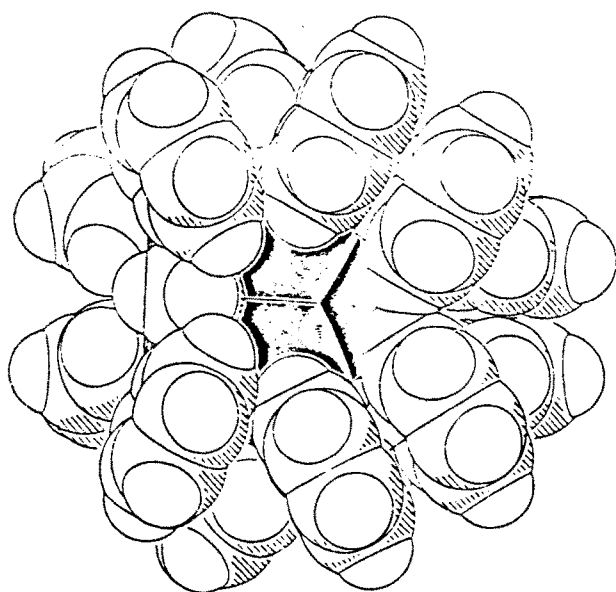


Figure 2. Space-filling diagram for the $[Pt_3(ReO_3)(\mu\text{-dppm})]^+$ cation in **2**. Here and in Figure 3 the platinum atoms are shown in black and the oxygen atoms are dotted. The cation is viewed along the normal to the Pt_3 plane from the side containing the $[ReO_4]^-$ anion which is not shown.

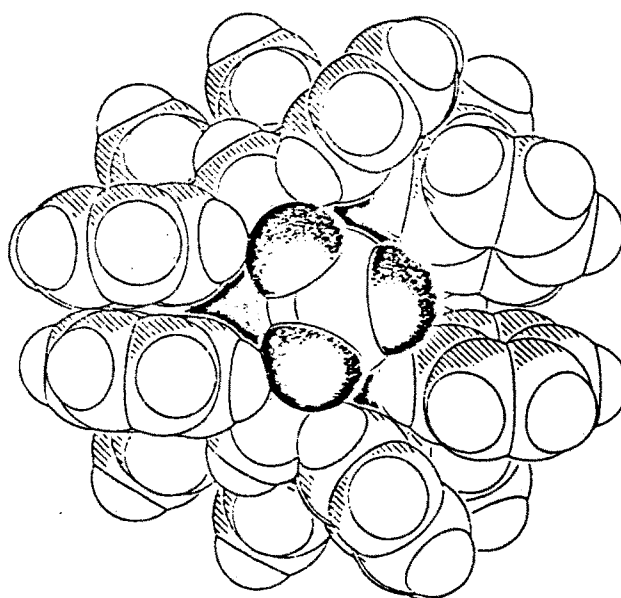


Figure 3. Space-filling diagram for the cation in **2**. Viewed normal to the Pt_3 plane from the ReO_3 side.

complexes contain cyclopentadienyl ligands [3], the preparation of other Pt_3 fragments based on oxide clusters should be feasible.

Experimental Section

All X-ray measurements were made at 23°C using a small block-shaped crystal. The accuracy of the analysis has been adversely affected by the high mosaicity and low diffracting power of the crystal specimen. Three reflections, $(-1\ 7\ 1, 4\ 5\ 10$ and $-7\ -1\ 4)$, were used to monitor the stability of the crystal and diffractometer. Their mean intensity showed a linear decline of up to 7.3% over the 144 hours of data collection. Empirical absorption corrections were made by the method of Walker & Stuart [14] at the end of the isotropic refinement. The internal agreement factor, R_{int} , for merging 566 duplicate intensities was 0.039 before and after correction for absorption. The structure was solved by the heavy atom method. The positions of the non-hydrogen atoms were obtained using Patterson and difference Fourier methods. The isotropic U_{ij} parameters are extremely large for some of the carbon atoms of rings **B** and **K**; this suggests positional disorder of these rings although alternative atomic sites were not obvious from difference maps. Crystallographic data for compound **2** is given in Table 2.

Table 2. Crystallographic data for $[Pt_3(ReO_3)(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)] [ReO_4]$

Empirical formula	$C_{75}H_{66}O_7P_6Pt_3Re_2$
Formula weight	2222.8
Space group	$P\bar{1}$
a, Å	14.154(4)
b, Å	14.213(3)
c, Å	20.522(4)
α , deg.	78.938(14)
β , deg.	75.812(19)
γ , deg.	74.957(22)
V, Å ³	3828.9(15)
Molecules in unit cell	2
Dcalc, g cm ⁻³	1.928
Crystal dimensions, mm	0.20 × 0.18 × 0.15
Temperature, °C	23
Radiation	MoK α
Wavelength, Å	0.71073
$\mu(\text{MoK}\alpha)$, cm ⁻¹	88.8
Data collection range, θ (deg.)	3.1-26.3
Absorption factors (on F)	0.78-1.32
Unique reflections	
with $I \geq 3\sigma(I)$	5414
Parameters refined	284
Discrepancy factor, R	0.069
R_w	0.077
Largest shift/esd ratio	0.07
Range of values in final difference synthesis, eÅ ⁻³	2.4 to -2.0

The GX program package [11] was used for all calculations; atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray crystallography (1992).

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