Models for Surface Catalysis: A Remarkable Pt₃(ReO₃) Cluster Cation

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Metal–metal bonded clusters may occur with the metal atoms in either high oxidation states, where the ligands are typically π-donors such as halide, alkoxide, oxide, or sulfide, or in low oxidation states, where the ligands are typically π-acceptors such as CO, isocyanides, or phosphines.[1] These two classes of metal clusters have little in common and are usually treated separately.[1,2] In particular, "hybrid" metal clusters containing both types of metal–ligand fragments are essentially unknown, although there are now several binuclear complexes with two metals in different oxidation states.[1–4] This is unfortunate since clusters containing both metal oxide and metal π-acceptor ligand fragments could not only display unique chemistry but also provide insights into the interaction of metal cluster surfaces with oxide materials in areas such as heterogeneous catalysis. This article reports the synthesis and structure of the cluster cation [Pt₃(ReO₃)(μ-dppm)₃]⁺ (1, dppm = Ph₂PCH₂PPh₂), which contains both a high oxidation state ReO₃ fragment and a low oxidation state Pt₃(μ-dppm)₃ unit. The stability of this new cluster suggests that a much wider spectrum of "hybrid" clusters might exist. The cluster is also interesting as a model for possible Pt–Re bonding and metal–support interactions in the important heterogeneous bimetallic Pt–Re/Al₂O₃ catalysts.[5]

The cluster cation [Pt₃{Re(CO)₃}(μ-dppm)₃]⁺ (2) is known to react with Me₃NO or O₂ at room temperature to give the oxidized clusters [Pt₃{Re(CO)₃}(μ₃-O)(μ-dppm)₃]⁺ (3) and [Pt₃{Re(CO)₃}(μ₃-O)₂(μ-dppm)₃]⁺ (4), respectively.[4] It has now been shown that the reaction of 2[PF₆] in refluxing o-xylene with O₂ gives 4[PF₆], which reacts further with O₂ to give the remarkable cluster 1[PF₆]. More extended reflux resulted in partial decomposition and formation of 1[ReO₄].[4]

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(3) Several carbonyl clusters containing one or two oxide ligands are known, but in all cases the oxide is present as a μ₃ ligand, not as an identifiable metal oxide fragment. Ge, Y.-W.; Sharp, P. R. *Inorg. Chem.* **1992**, *31*, 379.

(4) Xiao, J.; Vittal, J. J.; Puddephatt, R. J.; Manojlović-Muir, K. W. *J. Am. Chem. Soc.* **1993**, *115*, 7882. In one experiment using refluxing xylene, the yield of 1[PF₆] was ca. 90% after 7 h and the yield of 1[ReO₄] was ca. 30% after 15 h.

(5) Klabunde, K. J.; Li, Y.-X. Clusters, Alloys, and Poisoning, An Overview. In *Selectivity in Catalysis*; Davis, M. E., Suib, S. L., Eds.; ACS Symposium Series 517, American Chemical Society: Washington, DC, 1993.

(6) Spectroscopic and X-ray data for [Pt₃(ReO₃)(μ-dppm)₃][ReO₄] (1[ReO₄]): triclinic, P1̄; a = 14.154(4), b = 14.213(3), and c = 20.522(4) Å; α = 78.938(14)°, β = 75.812(19)°, and γ = 74.957(22)°; V = 3828.9(15) Å³, Z = 2; Enraf-Nonius CAD4 diffractometer with Mo Kα radiation, λ = 0.71073 Å; R = 0.069, Rw = 0.077 for 284 parameters and 5414 reflections with I ≥ 3σ(I). IR (Nujol mull): ν(Re≡O) (ReO₄⁻) = 915 (st), 905 (m); ν(Re≡O) (ReO₃) = 940 (w), 890(st). ³¹P NMR (CD₂Cl₂): δ –2.8 [s, ¹J(PtP) = 3134, ³J(PP) = 133 Hz].

Table 1. Comparison of Metal–Metal Distances (Å) in 1, 2, and 4

	1	2	4
Pt(1)–Pt(2)	2.598(2)	2.611(1)	2.826(1)
Pt(1)–Pt(3)	2.609(3)	2.593(1)	3.094(1)
Pt(2)–Pt(3)	2.600(3)	2.608(1)	3.081(1)
Pt(1)–Re	2.720(3)	2.684(1)	2.843(1)
Pt(2)–Re	2.748(3)	2.649(1)	2.854(1)
Pt(3)–Re	2.711(3)	2.685(1)	3.228(1)
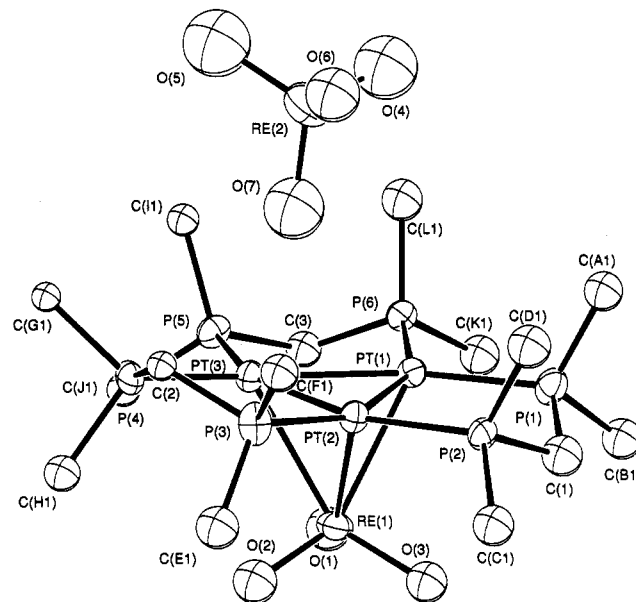
Figure 1. View of the [Pt₃(ReO₃)(μ-dppm)₃]⁺ cation and its associated [ReO₄]⁻ anion. 50% probability ellipsoids are displayed. For clarity, hydrogen atoms are omitted, as are all but the *ipso* carbon atom of each of the 12 phenyl rings. The range of Pt–P distances is 2.274(9)–2.306(9) Å. Metal–oxygen distances are 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), and Re(2)–O(7) 1.68(4) Å.
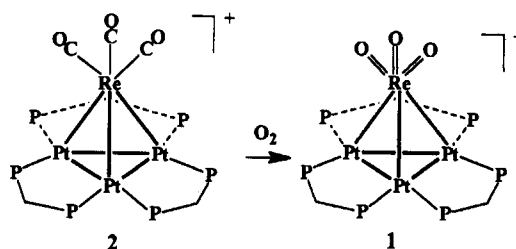
The structure of 1[ReO₄] has been determined by X-ray diffraction (see Table 1 and Figure 1).[6] The crystals contain [Pt₃(ReO₃)(μ-dppm)₃]⁺ cluster cations based on a tetrahedral Pt₃Re core. Each Pt–Pt edge is bridged by a dppm ligand, forming the well-known latitudinal Pt₃(μ-dppm)₃ moiety. A face of the Pt₃ triangle is μ₃-bridged by the Re(1)O₃ unit. Re(1) thereby adopts a highly distorted octahedral coordination which retains local C₃ symmetry, with Pt–Re(1)–Pt angles of 56.7(1)–57.4-(1)° and O–Re(1)–O angles of 104(1)–110(1)°. Thus 1 is closely related structurally to 2, with oxo ligands replacing carbonyl. The Pt–Pt distances in both 1 and 2 are nearly constant, and their means [2.602(4) and 2.604(6) Å] are virtually identical. The Pt–Re distances in each cluster are rather less regular, and the mean Pt–Re distance in 1 [2.726(11) Å] is somewhat greater than the corresponding mean [2.673(12) Å] for 2. The Re(1)–O distances in 1 [1.70(3)–1.77(3) Å] are unexceptional.[7]

(7) The mean length of 54 terminal Re–O (oxo) bonds is 1.709 Å. *International Tables for Crystallography*, Volume C, International Union of Crystallography; Kluwer Academic Publishers: Dordrecht, 1992; p 745.
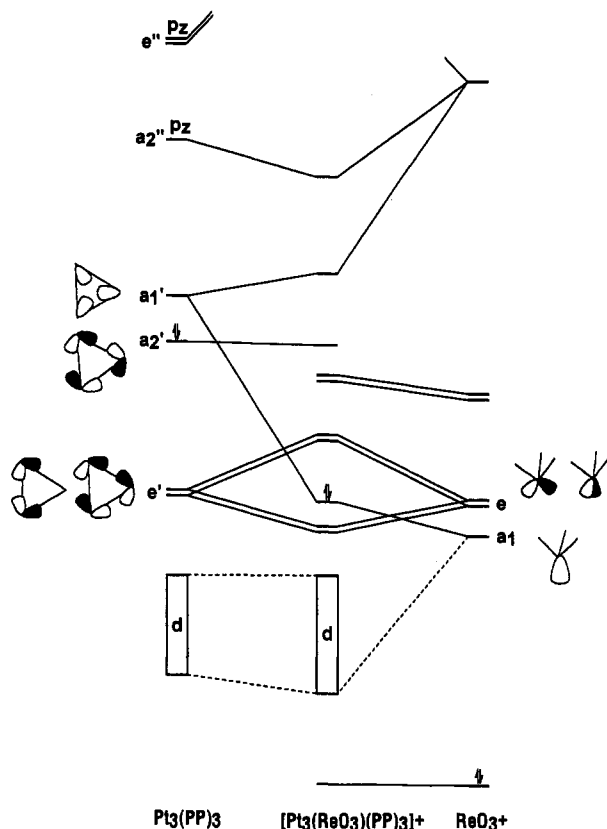
Figure 2. Qualitative MO correlation diagram for formation of the cation 1 from the fragments $Pt_3(\mu\text{-}H_2PCH_2PH_2)_3$ and ReO_3^+. The three highest energy occupied MOs are the M–M bonding orbitals of a_1 and e symmetry, while the LUMO is the M–M antibonding level of e symmetry.

Each cation in 1[ReO4] has closely associated with it a [ReO₄]⁻ anion which blocks the free face of the Pt₃ triangle: the Re(2) atom is nearly equidistant from Pt(2) and Pt(3) (4.97 and 4.96 Å) and is slightly further (5.29 Å) from Pt(1); the anion is oriented so that the Re(2)–O(7) vector points toward the midpoint of Pt(2)–Pt(3). The resulting short O(7)⋯Pt contacts, respectively 3.98, 3.41, and 3.37 Å, are, however, clearly nonbonding. We have previously noted the ability of the free face of a latitudinal Pt₃(μ-dppm)₃ (M = Pt, Pd) moiety to encapsulate a loosely bound anion: for example, above the free Pd₃ face of [Pd₃(μ₃-CO)(μ-dppm)₃]²⁺ there is an associated CF₃CO₂⁻ anion which participates in Pd⋯O contacts of 2.77(1)–2.92(2) Å, rather shorter than the Pt⋯O(7) contacts described here.[8] In the IR spectrum (Nujol mull) of 1[ReO₄], two bands at 915 and 905 cm⁻¹ could be assigned to ν(Re=O) of coordinated ReO₄⁻ (free ReO₄ gives only one band).[9] In addition, two bands due to ν(Re=O) in the Re(=O)₃ fragment were present at 940 and 890 cm⁻¹ in both 1[PF₆] and 1[ReO₄]. For comparison, the complex [(η⁵-C₅Me₅)Re(O)₃] gives ν(Re=O) at 909 and 878 cm⁻¹.[10] The ¹H and ³¹P NMR spectra of 1[PF₆] and 1[ReO₄] in CD₂Cl₂ solution were identical, indicating that the ReO₄⁻ ion is probably not associated with 1 in solution.[6,11]

The overall transformation of 2 to 1 involves the replacement of the three carbonyl ligands in 2 by the three terminal oxo ligands in 1. Since both CO and the terminal oxo ligand are formally two-electron donors, the overall cluster counts in 1 and 2 are the same. Both 1 and 2 are coordinatively unsaturated 54-electron

clusters, and it is therefore expected that the cluster cores should be similar. In contrast, cluster 4 is formed by the addition of two μ₃-O ligands to 2 without carbonyl dissociation and is a 62-electron cluster with much weaker metal–metal bonding.[4]

The bonding in 1 and 2 can be understood in terms of the donation of electron density from the three filled Pt–Pt bonding orbitals, having $a_1 + e$ symmetry, of the Pt₃(dppm)₃ fragment to the three vacant acceptor orbitals, also having $a_1 + e$ symmetry, of a Re(=O)₃⁺ fragment as shown in Figure 2. In this formalism, the platinum and rhenium atoms in 1 may be considered as Pt(0) and Re(VII). Even though this is an extreme interpretation, the oxidation states of platinum and rhenium in 1 are clearly very different to an extent which is unprecedented in transition-metal clusters.

The ReO₃ fragment is present in several other unusual compounds, such as MeReO₃, [(η⁵-C₅Me₅)ReO₃], and [(Me₂-PCH₂PMe₂)₂Cl₂Re-ReO₃], and the first two are considered as Re(VII) complexes.[2b,10] There is a useful analogy between complexes 1 and [(η⁵-C₅Me₅)ReO₃], since the donor orbitals of both the Pt₃(dppm)₃ fragment and the C₅Me₅⁻ ligand have $a_1 + e$ symmetry and so may be considered to be isolobal.[12] The analogy, together with the proven compatibility between the ReO₃⁺ and Pt₃(μ-dppm)₃ fragments, suggests several other possible target "hybrid" clusters, by substitution of Pt₃(dppm)₃ units for C₅Me₅⁻ ligands in known (C₅Me₅)MXₙ complexes and hence that the study of such "hybrid" clusters could become a major field of research. Specifically, since the vast majority of organometallic oxo complexes contain cyclopentadienyl ligands,[13] the preparation of other Pt₃ fragment-based oxide clusters should be feasible.

The oxidation sequence of 2 to 3 to 4 to 1 and then [ReO₄]⁻ shows how a low oxidation state rhenium atom can be oxidized to perrhenate in a stepwise manner while bound to a Pt₃ triangle. It is interesting that the reverse transformation has been proposed for the platinum-catalyzed reduction of rhenium oxides in the formation of the important reforming catalyst Pt–Re/Al₂O₃.[14] It has been suggested that rhenium oxides such as [ReO₄]⁻ migrate over the support surface and are reduced in contact with a platinum particle, whereupon bimetallic Pt–Re clusters are formed.[14] The mechanisms of the cluster and surface reactions may well be related, and complex 1[ReO₄] contains two types of Pt₃⁻rhenium oxide interactions which may be considered as models for proposed surface intermediates.

Supplementary Material Available: Crystallographic data for [Pt₃(ReO₃)(μ-Ph₂PCH₂PPh₂)₃][ReO₄] and tables of atomic parameters, anisotropic displacement parameters, bond lengths, and bond angles (13 pages); observed and calculated structure factors (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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