Addition of Oxygen to a Pt_3Re Cluster Complex: A Model for Dissociative Chemisorption of Oxygen

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This article reports the first example of the oxidative addition of dioxygen to a transition-metal cluster to give a bis(μ_3-oxo) cluster. Remarkably, this reaction leads to 4-electron oxidation of the cluster and an increase in the cluster electron count of 8-electrons, and it provides a simple model for the dissociative chemisorption of oxygen at a metal surface. This work adds significantly to the known value of organometallic oxo clusters as structural models for inorganic oxides and surface-bound oxide and to recent research on the dissociative addition of oxygen to multiply bonded dirhenium complexes.[1,2]

The coordinatively unsaturated cluster cation $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ (**1**), dppm = $Ph_2PCH_2PPh_2$, has been shown to be a good model for chemisorption of several small molecules at a Pt(111) surface,[3] but it fails to react with O_2. Since bimetallic Pt–Re catalysts may be more useful than platinum alone, it was of interest to prepare coordinatively unsaturated platinum–rhenium clusters as models for reactivity at the Pt/Re surface. Reaction of **1** with $[Re(CO)_5]^-$ gave the new cluster cation $[Pt_3\{Re(CO)_3\}(\mu\text{-dppm})_3]^+$ (**2**).[4] The cluster **2** was obtained as red-black crystals with either PF_6^- or BPh_4^- anions, and the structure of **2** as the $[BPh_4]$ salt is shown in Figure 1.[4] The cluster core has tetrahedral geometry, and the metal–metal bonds are short and presumably strong (Table I).

The cluster cation **2** has a valence electron count of only 54 and so is coordinatively unsaturated.[5] The simplest interpretation of the bonding in **2** is that the three filled M–M bonding orbitals (a_1 + e symmetry) of a $Pt_3(\mu\text{-dppm})_3$ fragment act as donors to the three vacant acceptor orbitals (also a_1 + e symmetry) of a $Re(CO)_3^+$ fragment.[6,7] In this way, each Pt atom shares 16 and the Re atom shares 18 valence electrons. However, several small molecules such as CO and HC≡CH add rapidly to **2** at the rhenium center to give $[Pt_3\{Re(CO)_3L\}(\mu\text{-dppm})_3]^+$, indicating that rhenium is the major site of unsaturation.

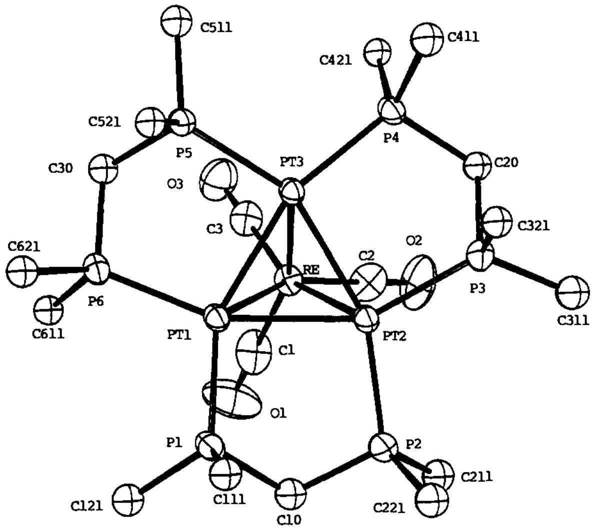

Figure 1. View of the structure of the cluster cation **2**. Only the ipso carbon atoms of the dppm phenyl groups are shown. The ranges of Pt–P and Re–C distances are 2.279(3)–2.293(3) and 1.85(1)–1.88(1) Å, respectively.

Table I. Comparison of Metal–Metal Distances (Å) in **2** and **3**[a]

	2	3
Pt(1)–Pt(2)	2.611(1)	2.826(1)
Pt(1)–Pt(3)	2.593(1)	3.094(1)
Pt(2)–Pt(3)	2.608(1)	3.081(1)
Pt(1)–Re	2.684(1)	2.843(1)
Pt(2)–Re	2.649(1)	2.854(1)
Pt(3)–Re	2.685(1)	3.228(1)

[a] The accepted range for Pt–Pt bonded distances is 2.6–2.8 Å, and values for **1** are 2.613(1)–2.650(1) Å. Previous values for *d*(Pt–Re) fall in the range 2.71–2.91 Å, with almost half in the range 2.83–2.87 Å. The Pt–Re distances in **2** appear to be the shortest known.[9]

Of particular interest is the reaction of O_2 with solutions of **2** to give the orange dioxo cluster $[Pt_3\{Re(CO)_3\}(\mu_3\text{-O})_2(\mu\text{-dppm})_3]^+$ (**3**).[8] This reaction takes several days to reach completion for solutions standing under 1 atm of air at room temperature, and no intermediates can be detected by NMR; the reaction is faster under pure O_2, while **2** is stable under a N_2 atmosphere. Remarkably, the same product **3** is formed by reaction of O_2 with **2** in the solid state. The structure of the cation **3** was established by an X-ray structural analysis of the PF_6^- salt and is illustrated in Figure 2.[8]

The inner core of **3** contains a slightly distorted tetrahedron of metal atoms in which two Pt_2Re faces are now capped by μ_3-oxo bridging atoms in a nearly symmetric fashion. The incorporation of two μ_3-O capping units is accompanied by a

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(1) (a) Ingham, S. L.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1993**, 166. (b) Schauer, C. K.; Voss, E. J.; Sabat, M.; Shriver, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 7662. (c) Chi, Y.; Hwang, L. S.; Lee, G. H.; Peng, S. M. *J. Chem. Soc., Chem. Commun.* **1988**, 1456. (d) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kober, E. M. *Inorg. Chem.* **1985**, *24*, 241. (e) Cotton, F. A.; Lahuerta, P.; Sanau, M.; Schwotzer, W. *J. Am. Chem. Soc.* **1985**, *107*, 8284. (f) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339. (g) Gland, J. L.; Sexton, B. A.; Fisher, G. B. *Surf. Sci.* **1980**, *95*, 587. (h) Zaera, F.; Somorjai, G. *Surf. Sci.* **1985**, *154*, 303. (i) Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* **1983**, 246. (j) Bartley, S. L.; Dunbar, K. R.; Shih, K.-Y.; Fanwick, P. E.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1993**, 98.

(2) (a) Ceriotti, A.; Resconi, L.; Demartin, F.; Longoni, G.; Manassero, M.; Sansoni, M. *J. Organomet. Chem.* **1983**, *249*, C35. (b) Lavigne, G.; Lugan, N.; Bonnet, J. J. *Nouv. J. Chim.* **1981**, *5*, 423.

(3) Puddephatt, R. J.; Manojlović-Muir, Lj.; Muir, K. W. *Polyhedron* **1990**, *9*, 2767.

(4) Spectroscopic and X-ray data for **2** are as follow. IR (Nujol): ν(CO) 1979s, 1873s, 1867s. ^{31}P NMR (CD_2Cl_2): δ 7.9 [s, $^1J(PtP) = 2411$, $^2J(PtP) = 248$, $^3J(PP) = 198$ Hz]. $[Pt_3Re(CO)_3(\mu\text{-dppm})_3][BPh_4]\cdot CH_2Cl_2$: triclinic, $P\bar{1}$; $a = 21.278(3)$, $b = 19.021(5)$, and $c = 11.352(2)$ Å, $\alpha = 90.10(2)°$, $\beta = 99.83(1)°$, $\gamma = 94.31(2)°$, $V = 4514(2)$ Å^3, $Z = 2$; Enraf-Nonius CAD4 diffractometer with Mo Kα radiation, $T = -50$ °C, $\lambda = 0.710\,73$ Å; $R = 0.037$, $R_w = 0.030$ for 392 parameters and 8885 reflections with $I \geq 2.5\sigma(I)$. Anal. Calcd for $C_{103}H_{88}BCl_2O_3P_6Pt_3Re$: C, 51.3; H, 3.7. Found: C, 51.3; H, 3.6.

(5) Mingos, D. M. P.; May, A. S. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990. The most common electron count for tetrahedral clusters is 60, such as in $[Ir_4(CO)_{12}]$.

(6) EHMO calculations on the model cluster $[Pt_3\{Re(CO)_3\}(\mu\text{-}H_2PCH_2PH_2)_3]^+$ provide support for the filled cluster MOs having a_1 + e symmetry, there being only three skeletal electron pairs.

(7) For previous theoretical work on Pt_3L_6 clusters and on $M(CO)_3$ fragments, see (a) Evans, D. G. *J. Organomet. Chem.* **1988**, *352*, 397. (b) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; Chapter 20.

(8) Data for **3** are as follow. IR (Nujol): ν(CO) 1974s, 1862s, 1852s. ^{31}P NMR (CD_2Cl_2): δ 3.6 [m, $^1J(PtP) = 2770$ Hz], 3.3 [s, $^1J(PtP) = 3462$ Hz], 0.7 [m, $^1J(PtP) = 3960$ Hz]. $[Pt_3Re(\mu_3\text{-O})_2(CO)_3(\mu\text{-dppm})_3][PF_6]\cdot OEt_2$: monoclinic, $P2_1/n$; $a = 17.1603(18)$, $b = 23.2822(17)$, and $c = 19.7021(9)$ Å, $\beta = 94.160(6)°$, $V = 7850.8(11)$ Å^3, $Z = 4$; Enraf-Nonius CAD4 diffractometer with Mo Kα radiation, $\lambda = 0.710\,69$ Å; $R = 0.047$, $R_w = 0.042$ for 802 parameters and 11822 reflections with $I \geq 2\sigma(I)$. Anal. *Calcd* for $C_{82}H_{76}F_6O_6P_7Pt_3Re$: C, 43.6; H, 3.4. Found: C, 43.3; H, 3.2.

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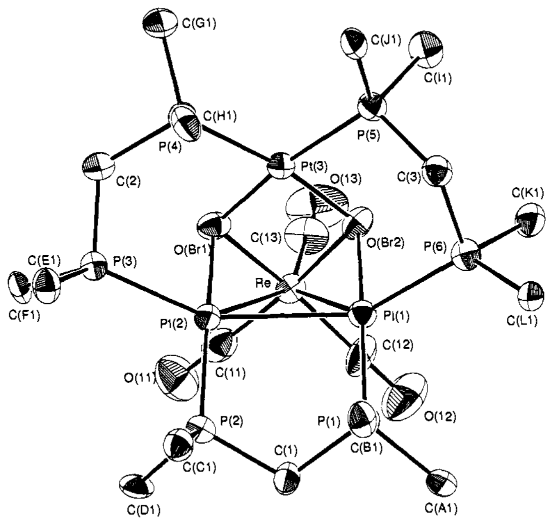
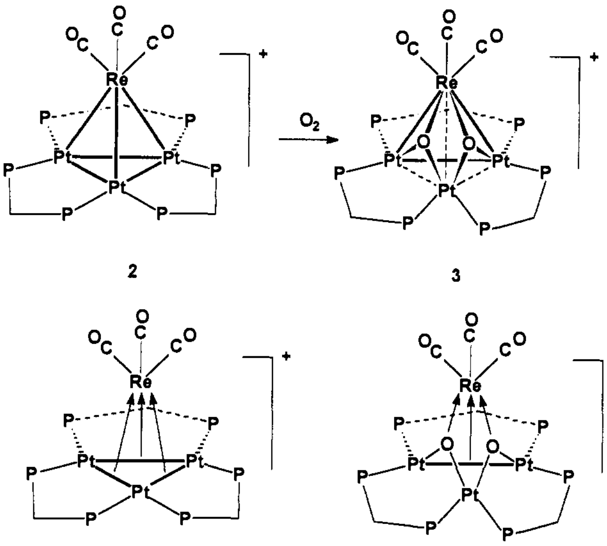


Figure 2. View of the cluster cation 3, showing 50% probability ellipsoids. Only the ipso carbon atoms of the dppm phenyl groups are shown. The ranges of Pt-P and Re–C distances are 2.227(3)–2.243(3) and 1.89(1)–1.89(1) Å, respectively. Metal–oxygen distances are Pt(1)–O(Br2) 2.049(6), Pt(2)–O(Br1) 2.065(6), Pt(3)–O(Br1) 2.036(6), Pt(3)–O(Br2) 2.046(6), Re–O(Br1) 2.117(6), and Re–O(Br2) 2.121(6) Å.

significant lengthening of all the metal–metal distances compared to those in **2** (Table I). The distances within the Pt(1)Pt(2)Re triangle are still clearly in the bonding region, but the Pt(1)···Pt(3), Pt(2)···Pt(3), and Pt(3)···Re distances are borderline or nonbonding.[9] In contrast, a μ_3-oxo ligand causes shortening of metal–metal bonds in some other clusters, where the electron count does not change.[2] Since a μ_3-O ligand donates 4 electrons, the electron count in **3** is 62, compared to only 54 in **2**, and so cleavage of M–M bonds is expected.[5] The bonding in **3** may be described in terms of two 16-electron Pt(I) atoms, Pt(1) and Pt(2), having similar distorted square-planar $PtOP_2$ centers with a Pt(1)–Pt(2) bond, a square-planar 16-electron Pt(II) atom, Pt(3), with a *cis*-PtO_2P_2 center, and an octahedral *fac*-Re(I)-$(O)_2(CO)_3$ center which completes an 18-electron configuration by accepting two electrons from the Pt(1)–Pt(2) bond. The valence bond representations of **2** and **3** are then clearly related (Scheme I) and may be used to rationalize the remarkable increase in electron count without any ligand dissociation. A similar bonding scheme has been proposed for the dioxo-capped cluster $[Pt_4Cl_2(\mu_3\text{-}O)_2(dmso)_6]$ (dmso = dimethyl sulfoxide).[10]

Scheme I (Top) Formation of **3**; (bottom), Simplified VB Representations



Cluster **3** was also formed when **2** was treated with the oxygen atom donor Me_3NO in the absence of O_2. Interestingly, an intermediate cluster **4** was detected by NMR in this reaction and is tentatively suggested to be the mono-oxo adduct.[11] No such intermediate was detected in the reaction of **2** with O_2, and, together with the observation that the reaction also occurs with **2** in the solid state, this strongly suggests that the formation of **3** from **2** and O_2 occurs by a concerted mechanism. It is likely that O_2 first adds to the rhenium center, and then O–O bond cleavage occurs as the oxygen atoms migrate to the Pt_2Re faces. There is a remarkable resemblance to chemisorption, which leads to $M_3(\mu_3\text{-}O)$ units on either platinum or rhenium surfaces and, at least for platinum, is thought to occur via an intermediate O_2 complex.[1g,h] Of course, the ability of metal surfaces to bind oxygen is important in catalytic oxidation reactions, and so it is also significant that **2** is a catalyst for the oxidation of Ph_3P to $Ph_3P{=}O$ by O_2 (turnover number at room temperature = 1 mol(mol **2**)$^{-1}$ h^{-1}). Clearly the type of $Pt_2Re(\mu_3\text{-}O)$ units established in this work could also be present in oxide supported bimetallic Pt–Re catalysts.

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Supplementary Material Available: Tables of X-ray structural data for **2** and **3** (34 pages); observed and calculated structure factors for **2** and **3** (85 pages). Ordering information is given on any current masthead page.

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(9) (a) Douglas, G.; Manojlović-Muir, Lj.; Muir, K. W.; Rashidi, M.; Anderson, C. M.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 6527 and references therein. (b) Ciani, G.; Moret, M.; Sironi, A.; Antognazza, P.; Beringhelli, T.; D'Alfonso, G.; Pergola, R. D.; Minoja, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1255. The Cambridge Structure Database yielded references to 15 structures containing Pt-Re bonds.

(10) Betz, P.; Bino, A. *J. Am. Chem. Soc.* **1988**, *110*, 602.

(11) Data for **4** are as follow. IR (Nujol): ν(CO) 1978s, 1864s,br. ^{31}P NMR (CD_2Cl_2): δ 11.7 [m, $^1J(PtP)$ = 2709 Hz], 11.4 [m, $^1J(PtP)$ = 2430 Hz], 1.5 [m, $^1J(PtP)$ = 4178 Hz].