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Pt_5Re Cluster That Models a Bimetallic Catalyst: Evidence for PtRe Multiple Bonding

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The nature of the important bimetallic $Pt-Re-Al_2O_3$ catalysts used in petroleum reforming continues to be a controversial though thoroughly studied subject. The most recent study of which we are aware suggests that the platinum and rhenium are present mostly as Pt particles and ReO_2, respectively, and that ReO_2 acts by modifying the alumina surface.[1] One popular theory is that the oxophilic rhenium binds tightly both to the alumina substrate and to the microscopic particles of platinum, thus anchoring these particles to the oxide surface and minimizing their aggregation to larger particles, which is one cause of catalyst deactivation.[2] One way of mimicking such O−Re−Pt interactions is by binding rhenium oxide fragments to suitable platinum cluster complexes,[3] and this paper reports a remarkable bimetallic cluster complex derived from such a reaction. In has an interesting structure, with distinct oxide and carbonyl faces; it exhibits very unusual metal−metal bonding; and it provides perhaps the best model yet known for an alumina−rhenium oxide−platinum interface.

The reaction of the cluster $[Pt_3(\mu\text{-CO})_3L_3]$, L = P(cyclohexyl)$_3$, with Re_2O_7 is complex, but the new cluster $[Pt_5(CO)_5L_4Re(\mu\text{-O})_3(\mu\text{-OH})(ReO_4)][ReO_4]$, **1**, could be crystallized from the crude product mixture in about 25% yield[4] and was characterized by an X-ray structure determination and spectroscopically.[4,5] The structure of the cation is shown in Figure 1. There is a central RePtCO unit with four peripheral Pt(CO)L units, each of which is coplanar with and arranged like spokes of a wheel around the Re−Pt axis, and each peripheral PtRe unit is bridged by a μ-O or μ-OH ligand. There is a perrhenate ligand very weakly bonded to the central rhenium atom. It is then immediately obvious that, ignoring metal−metal bonding, the central rhenium is ligated only by hard oxygen donors and the central platinum only by soft carbonyl, while the peripheral platinums have mixed Pt(CO)(L)(O) coordination. The result is that, viewed from the rhenium side of the wheel, there is an array of oxygen donors, and from the platinum side, an array of carbonyls, with the phosphine ligands at the interface. It is easy to envision the rhenium incorporated into an oxide surface and binding to a platinum crystallite in a similar way in a $Pt/Re/Al_2O_3$ catalyst.

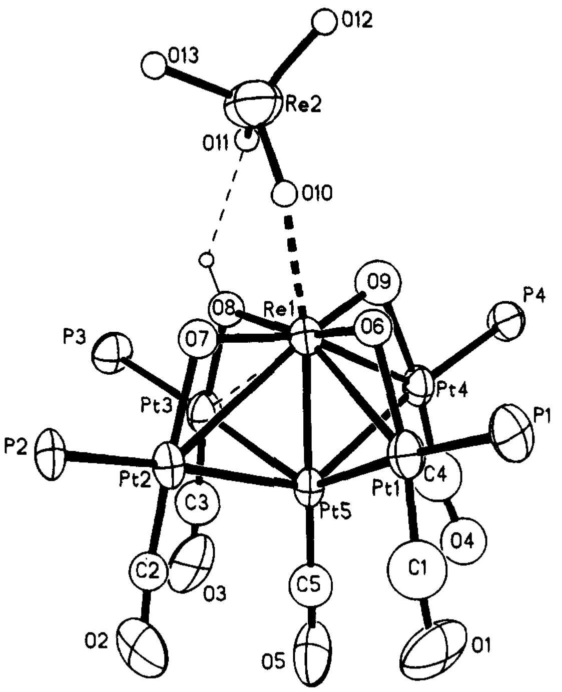

Figure 1. View of the structure of the cation $[Pt_5(CO)_5L_4Re(\mu\text{-O})_3(\mu\text{-OH})(ReO_4)][ReO_4]$, **1**, L = P(cyclohexyl)$_3$. The cyclohexyl groups are omitted for clarity. The OH proton was not directly located, and the atoms O(10)−O(13) are shown as spheres of arbitrary radius.[5]

The central Pt−Re bond in **1** at Re(1)−Pt(5) = 2.548(2) Å is the shortest such bond known. Most Pt−Re single bonds are in the range 2.8−2.9 Å, and the shortest previously reported is 2.65 Å.[3] In contrast, the oxygen-donor bridged RePt distances are in the range 2.792(2)−3.275(2), with the longest being tentatively assigned to the hydroxide-bridged bond.[5] The distances between the central and peripheral platinum atoms at 2.712(2)−2.782(2) Å are intermediate, and the distances between peripheral platinum atoms at 3.380(2)−3.714(2) Å are clearly nonbonding. The cluster electron count for **1** is 84 or 82 electrons, if the weakly bonded perrhenate ligand is included or excluded, respectively. The closest analogy of **1** with classical clusters would be to consider it to be formed by fusion of two butterfly clusters at a common edge, and the predicted electron count is then 92e.[6] The lower electron count is a common feature of both platinum clusters (Pt tends to have a 16e count) and clusters with π-donor ligands.[6]

EHMO calculations have been carried out on the model cluster $[Pt_5(CO)_5(PH_3)_4ReO_4]^+$, considered to be formed from **1** by replacement of the PCy_3 ligands by PH_3 and by removal of a weakly bound $HReO_4$.[7] It is inappropriate to discuss the details in this context, but the calculations do indicate at least

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(1) Huang, Z.; Fryer, J. R.; Park, C.; Stirling, D.; Webb, G. *J. Catal.* **1994**, *148*, 478.

(2) (a) Augustine, S. M.; Sachtler, W. M. H. *J. Catal.* **1989**, *116*, 184. (b) Gates, B. C. *Catalytic Chemistry*; Wiley: New York, 1992. (c) Meitzner, G.; Via, G. H.; Lytle, F. W.; Sinfelt, J. H. *Physica B* **1989**, *158*, 138.

(3) Xiao, J.; Puddephatt, R. J.; Manojlović-Muir, Lj.; Muir, K. W.; Torabi, A. A. *J. Am. Chem. Soc.* **1994**, *116*, 1129.

(4) Cluster **1** was prepared from equimolar amounts of $[Pt_3(\mu\text{-CO})_3L_3]$ and Re_2O_7 in THF at room temperature. The red solution turned to dark brown immediately. The mixture was stirred for 18 h and filtered through Celite, the solution was concentrated, and the product was precipitated by addition of hexane. Recrystallization from CH_2Cl_2/diethyl ether or acetone/hexane solution by diffusion gave the product as black crystals in 25% yield. Anal. Calcd for $C_{74}H_{143}O_{17}P_4Pt_5Re_3$: C, 30.0; H, 4.9. Found: C, 30.2; H, 4.8%. IR (Nujol): ν(CO) = 2068 (vs, br), 2036 (s), 2005 (s) cm^{-1}; ν(Re═O) = 927 (m), 911 (m, sh), 903 (s), 880 (m). NMR in CD_2Cl_2 at −90 °C: $\delta(^1H)$ = 3.60 [dd, 1H, *J*(PH) = 7 Hz, 3 Hz, ^2J(PtH) = 13 Hz, Pt(μ-O*H*)Re]; 1.89, 1.41 [m, br, PCy]; $\delta(^{31}P)$ = 48.5, 43.0, 40.1, 33.5 [br, each with ^1J(PtP) ca. 3600 Hz]. At room temperature the ^{31}P NMR gave a very broad singlet [δ = 38.9, ^1J(PtP) = 3628 Hz]; it appears that the phosphines are locked into an unsymmetrical conformation. The assignment of the OH proton was confirmed by spiking the sample with D_2O, when the peak disappeared while the rest of the ^1H and ^{31}P NMR spectra were unchanged. For other properties of the starting cluster, see: Imhof, D.; Venanzi, L. M. *Chem. Soc. Rev.* **1994**, 185.

(5) X-ray data for **1**·0.5Et$_2$O: orthorhombic, *Fdd*2 (No. 43), a = 27.783(5) Å, b = 55.20(1) Å, c = 26.778(7) Å, V = 41070(22) Å^3, Z = 16, R = 0.0688. Note that Pt and Re and O and OH are not easily distinguished by X-ray methods. The metal assignments are made on the basis of the spectroscopic data and by consideration of the bond angles and distances. The OH group is chosen as that with the longest Re−O bond; it happens that the ReO_4^- ligand leans in this direction and could be H-bonded to the OH group. An alternative picture, useful for bonding considerations, is to consider a $HReO_4$ molecule bound to both the central rhenium and a μ-O ligand.

(6) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1990.

(7) The geometry used in the EHMO calculations was based on an idealized version of the X-ray structure, with all Re−O, Pt−O, Re−Pt, and Pt−Pt distances equal, giving a complex with C_{4v} symmetry. Standard parameters were used for all atoms, as supplied with the program package CACAO.

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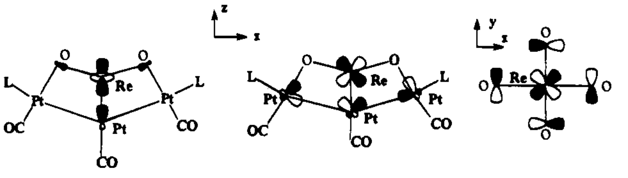
partial triple-bond character in the central Pt–Re bond, with complications due to the presence of peripheral metal–metal bonds. The electron configuration associated with the central PtRe bond may be considered as $\sigma^2\pi^4$ in which the σ-bond is formed by Re(d_{z^2})–Pt(sp_z) overlap, **A**, and the π-bonds by Re(d_{xz})–Pt(p_xd_{xz}) and Re(d_{yz})–Pt(p_yd_{yz}) overlap, **B**. Note that the symmetry of the molecule would also allow δ-bonding, but the calculations indicate that the Re(d_{xy}) level is the LUMO; it has π^*(ReO) character and has no significant interaction with the filled Pt(d_{xy}) level, **C**. Rhenium forms many multiple ReRe and ReM bonds, but there are no precedents for platinum–metal multiple bonding.[8] The very short central Pt–Re distance in **1** and the very unusual structure strongly suggest a degree of multiple metal–metal bonding consistent with the bonding hypothesis given.[8] The analogy between the cluster and catalyst then raises the intriguing question of whether RePt multiple bonding may also be present at the oxide–platinum crystallite interface in bimetallic catalysts. In this respect, it is interesting that the mean PtRe distance determined by EXAFS in the supported Pt–Re catalyst is 2.64 Å,[2c] longer than in **1** but shorter than any known Pt–Re single bond[3] and also shorter than the intermetallic distances in either platinum (2.775 Å) or rhenium (2.750 Å) metals.[2]



A, Re(d_z2)-Pt(s,p_z), σ

B, Re(d_{xz})-Pt(p_x,d_{xz}), π
(not shown) Re(d_{yz})-Pt(p_y,d_{yz}), π

C, Re(d_{xy})-O(p), π^*

Note: only coplanar atoms are shown for clarity

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Supporting Information Available: Summary of structure determination and Tables S1–S6, crystal data, positional parameters, bond parameters, thermal parameters, and H-atom coordinates (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet, see any current masthead page for ordering information and Internet access instructions.

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[8] Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Clarendon Press: Oxford, 1993.