

Models for Bimetallic Catalysts: Selectivity in Ligand Addition as a Function of Rhenium Oxidation State in Pt₃Re Clusters

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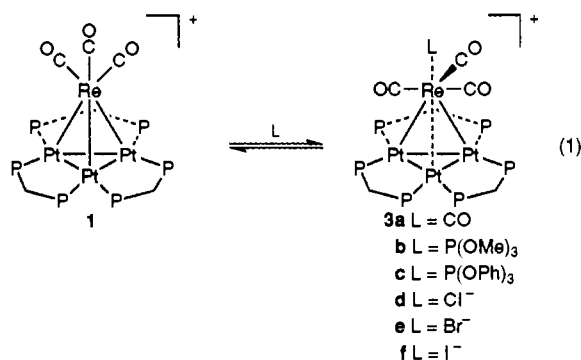
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The ligands CO, P(OR)₃, and X⁻ (X = Cl, Br, I) add selectively to the Re and Pt₃ sites in the coordinatively unsaturated clusters [Pt₃{Re(CO)₃}(μ-dppm)₃]⁺ and [Pt₃{ReO₃}(μ-dppm)₃]⁺ respectively, dppm = Ph₂PCH₂PPh₂: the selectivity thus displays a remarkable dependency on the oxidation state of rhenium.

Coordinatively unsaturated metal cluster complexes can act as models for heterogeneous surface catalysts, but models for the important bimetallic catalysts such as Pt/Re/Al₂O₃ are less developed.¹ In such oxide-supported catalysts, the metals may undergo reversible oxidation and reduction.² In the case of Pt/Re/Al₂O₃ catalysts, which are widely used for commercial reforming of petroleum,³ the platinum is always present as Pt⁰ but, for the more oxophilic rhenium, there is evidence for the presence of Re^{II} and Re^{IV} in addition to Re⁰.⁴ The coordinatively unsaturated clusters [Pt₃{Re(CO)₃}(μ-dppm)₃]⁺, **1**,⁵ and [Pt₃{ReO₃}(μ-dppm)₃]⁺, **2**,⁶ can act as models for surface Pt/Re clusters in which Re is in low and high oxidation states respectively.† Since both CO and the terminal oxo ligand are formally two-electron donors, the overall cluster count in **1** and **2** remains the same. Both are coordinatively unsaturated 54-electron clusters with tetrahedral Pt₃Re cores, but the oxidation states at rhenium are very different.⁶ This paper addresses the question of how the site selectivity for ligand addition depends on the oxidation state of rhenium as a model for possible selectivity in chemisorption to Pt/Re/Al₂O₃ bimetallic catalysts.

Cluster **1** reacts easily with donor ligands according to eqn. (1) to give the adducts **3** by selective addition to the rhenium centre.‡ The reactions of **1** with CO, and halides are reversible, and for the halides the equilibrium is shifted in favour of the products in the order I⁻ > Br⁻ > Cl⁻. All the adducts can be isolated as red solids and cluster **3c** was characterized by an X-ray structure determination.‡ The structure, Fig. 1, shows that the Pt₃Re core has distorted tetrahedral geometry. The mean Pt–Pt (2.60 Å in **1**, 2.64 Å in **3c**) and Pt–Re (2.67 Å in **1**, 2.84 Å in **3c**) distances are longer than in **1**, and the distance Pt(3)⋯Re = 2.942(1) Å in **3c** is especially long. These data indicate that the new Re–L bonding occurs at the expense of some cluster bonding. However, it should be noted that two of the carbonyl ligands on rhenium weakly semi-bridge to Pt(1) and Pt(2), a feature absent in **1**. The new clusters **3** are fluxional. For example, the ³¹P NMR spectrum of **3c** contained only one resonance due to dppm phosphorus atoms at room temperature but three resonances at low temperature, as expected for the solid state structure. The mechanism of fluxionality is proposed to involve the rotation of the Re(CO)₃L unit about the Pt₃ triangle.



The cluster complex **2** also reacts readily with donor ligands, but the reactions now occur at the Pt₃ centre according to eqn. (2). Carbon monoxide adds to **2** in a μ₃ mode to give **4a** whereas trimethyl phosphite acts as a terminal ligand to give **5**. Halide ions appear to give **4b–d** with Pt₃(μ₃-X) coordination since the ³¹P NMR spectrum gives only one resonance. However, the resonance is broader at low temperature and it is possible that these adducts have lower symmetry (for example with μ₂ or terminal X) but are fluxional. The reactions in eqn. (2) are all reversible. Thus, for example, CO is readily lost from **4a** to regenerate **2**, and halide exchange

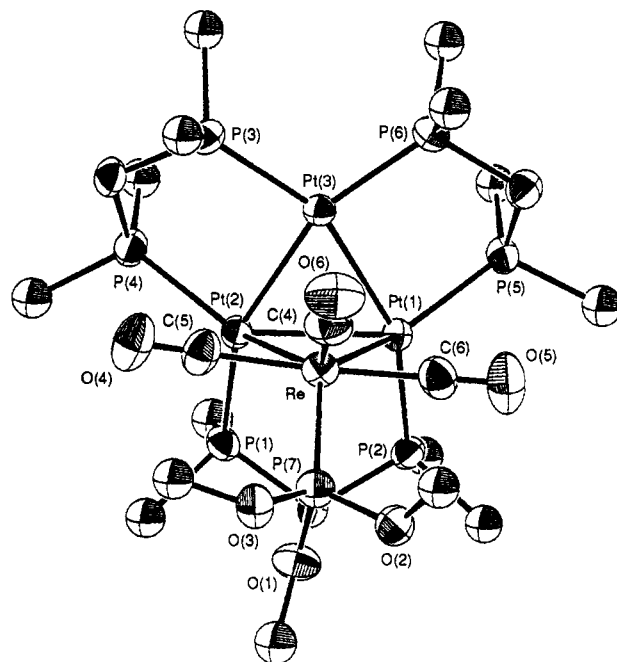
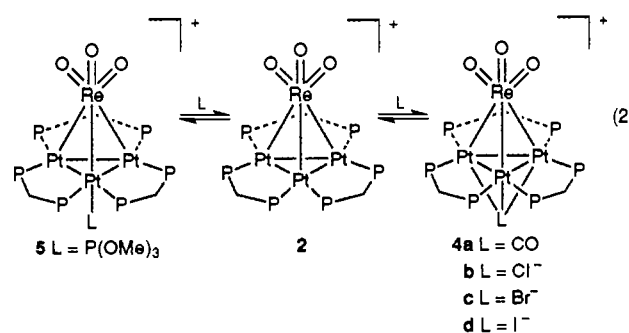


Fig. 1 A view of the [Pt₃{Re(CO)₃}(μ-dppm)₃]⁺ cation, **3c**. 50% probability ellipsoids are displayed. For clarity, hydrogen atoms are omitted as are all but the *ipso* carbon atom of each of the fifteen phenyl rings. Selected distances are: Pt(1)–Pt(2) 2.677(1), Pt(1)–Pt(3) 2.635(1), Pt(2)–Pt(3) 2.603(1), Pt(1)–Re 2.825(1), Pt(2)–Re 2.762(1), Pt(3)⋯Re 2.942(1), Pt(1)⋯C(6) 2.55(1), Pt(2)⋯C(5) 2.43(1), Re–P(7) 2.255(3), Re–C(4) 1.885(10), Re–C(5) 1.998(9), Re–C(6) 1.969(9), Pt–P 2.253(3)–2.307(2) Å.



reactions indicate that adduct formation is favoured in the order $I^- > Br^- > Cl^-$. The triply bridging carbonyl in **4a** is characterized in the IR by $\nu(\text{CO}) = 1606 \text{ cm}^{-1}$ and in the ^{13}C NMR by a 1:4:7:4:1 quintet at $\delta = 224.6$ with $^1J(\text{PtC}) = 513 \text{ Hz}$. The value of $\nu(\text{CO})$ is particularly low, indicating strong backbonding, but the other parameters are as expected for a $\text{Pt}_3(\mu_3\text{-CO})$ group.⁸ The terminal nature of the $\text{P}(\text{OMe})_3$ ligand in the adduct **5** is shown by the low temperature ^{31}P NMR spectrum, but the complex is fluxional due to easy migration of the phosphite ligand around the triangular Pt_3 face of the cluster.⁸ The coordination of the phosphite to platinum is shown by the magnitude of $^1J(\text{PtP}) = 3713 \text{ Hz}$, which can be compared to the coupling $^2J(\text{PtReP}) = 156 \text{ Hz}$ in **3b**. Triphenyl phosphite failed to react with **2**.

The contrast between the selectivities towards ligand addition of **1** and **2** is dramatic. The reactivity of **2** is similar to that of $[\text{Pt}_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$, and of related main group metal clusters such as those containing $\text{Pt}_3(\mu_3\text{-SnX}_3)$ or $\text{Pt}_3(\mu_3\text{-Hg})$ units, which all react selectively at the Pt_3 centre, sometimes with displacement of the main group metal.⁹ The different reactivity of **1** is noteworthy. If the argument that the $\text{Pt}_3(\mu\text{-dppm})_3$ fragment is isolobal to C_5H_5^- is accepted,⁶ then **1** may be considered isolobal to $[\eta^5\text{-C}_5\text{H}_5\text{Re}(\text{CO})_3]$. This complex is inert to ligand addition but the related complex $[\eta^5\text{-C}_5\text{H}_5\text{Re}(\text{CO})(\text{NO})\text{R}]$ is known to add ligands at Re with slippage of the $\eta^5\text{-C}_5\text{H}_5$ ligand to η^3 .¹⁰ The ligand addition to **1** could be considered analogous to this chemistry. In particular, the $\text{Re}(\text{CO})_3^+$ fragment has three acceptor orbitals and so can accept three electron pairs from the Pt–Pt bonding MO's of $[\text{Pt}_3(\text{dppm})_3]$ but $\text{Re}(\text{CO})_4^+$ has only two acceptor orbitals and so only two electron pairs can be accepted. The weakening of PtRe bonding in **3c** compared to **1** thus follows naturally. Of course, this does not explain the selectivity difference and future theoretical analysis is desirable for this purpose. In bimetallic catalysts, the selectivity of ligand binding could also change with the oxidation state of the metal clusters present. In the specific case of Pt/Re/ Al_2O_3 catalysts, there is evidence that Re^0 and Re^{IV} coexist on the surfaces of the reduced catalyst, and that, while Re^0 chemisorbs CO, Re^{IV} shows no such activity.^{4f} The selectivity towards ligand addition of the clusters **1** and **2** can be considered to model this effect. We know of no precedents for such a dramatic difference in selectivity towards ligand addition to clusters as a function of oxidation state of one of the metal centres.

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Footnotes

† In clusters **1** and **2**, the formal oxidation states of Re may be (I) and (VII) respectively and **2** is a rare example of a cluster with metals in very different oxidation states.^{5–7}

‡ Crystal data for $3c[\text{PF}_6] \cdot \text{EtOH}$, $\text{C}_{108}\text{H}_{187}\text{F}_6\text{O}_7\text{P}_8\text{Pt}_3\text{Re}$, $M = 2498.0$, triclinic, space group $P\bar{1}$, $a = 13.993(1)$, $b = 17.868(1)$, $c = 19.753(2)$ Å, $\alpha = 88.198(7)$, $\beta = 87.766(7)$, $\gamma = 72.394(4)^\circ$, $V = 4702.7(7)$ Å³, $Z = 2$, $D = 1.764 \text{ g cm}^{-3}$, $R = 0.041$, $R_w = 0.043$ for refinement of 464 parameters using 14,768 reflections with $I \geq 3\sigma(I)$ and $\theta(\text{Mo-K}\alpha) \leq 30^\circ$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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