

COORDINATIVELY UNSATURATED Pt AND Pt-Re CLUSTERS AS MODELS FOR SURFACES AND BIMETALLIC CATALYSTS

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ABSTRACT. The scope and limitations of the use of coordinatively unsaturated transition metal clusters as models for reactivity of metal surfaces in chemisorption and catalysis are outlined. The use of coordinatively unsaturated Pt₃ and Pt₃Re clusters as models for reactions in supported platinum or bimetallic platinum-rhenium catalysts is then outlined. Platinum-rhenium clusters are shown to have unique reactivity, particularly in sulfur or oxygen atom addition reactions.

1. Introduction

It is now recognized that chemisorption and the reactions occurring in heterogeneous catalysis are forms of coordination chemistry and organometallic chemistry of the metal surface and that parts of this chemistry can be modelled by using transition metal clusters. For example, in terms of reactions of metal surfaces and complexes respectively, non-dissociative chemisorption is like coordination and dissociative chemisorption is like oxidative addition¹. When CO binds to a platinum(111) surface, it can bind at on-top (terminal) or two-fold (doubly bridging) sites and perhaps also at three-fold (triply bridging) sites; the surface mobility of CO is due to easy migration between these sites². Such metal-carbonyl bonding modes are also common in metal cluster complexes, and the mobility of CO on metal surfaces is analogous to carbonyl fluxionality.^{1,2} Similarly, the dissociative chemisorption of dihydrogen on a metal surface is analogous to the oxidative addition of dihydrogen to a metal cluster complex. In each case, the H-H bond is cleaved and the resulting hydrogen atoms usually bind in bridging positions between two or three metal atoms^{1,2}. If the reactivity of a surface is to be mimicked in metal clusters, it will be necessary for the

clusters to be coordinatively unsaturated, having empty orbitals on as many metal atoms as possible to model the dangling orbitals of surface metal atoms which are available for easy ligand binding. The late transition elements and particularly Rh, Ir, Pd and Pt are suitable since these elements often form clusters in which the metal has the 16-electron configuration³. The major problem in developing the cluster-surface analogy with the late transition elements is that the metal-metal bonds in their cluster complexes undergo cluster fragmentation during many chemical reactions.³ There are excellent accounts of structure and bonding in these complexes, which rationalize these properties⁴.

In order to stabilize cluster complexes with respect to fragmentation, it is desirable to use bridging ligands which bind more strongly than the μ -CO, μ -RNC, μ -SO₂ or μ -H ligands which are typically present in platinum cluster complexes.³ The ligand Ph₂PCH₂PPh₂, dppm, has proved to be one of the most useful such bridging groups,⁰ and allowed the synthesis of a new class of trinuclear platinum clusters based on the [Pt₃(μ -dppm)₃] bridged triangular unit³.

2. Models for chemisorption on a platinum surface

The parent molecule [Pt₃(μ -dppm)₃] has not been synthesized but there have been studies of its chemical bonding, based on the combination of three *cis*-PtL₂ units. The three frontier orbitals of the PtL₂ unit are shown on the left of Figure 1; each fragment has an orbital available for tangential bonding, an orbital available for radial bonding and an empty 6p_z orbital in order of increasing energy, and there are two electrons available for metal-metal bonding in each fragment. In the hypothetical molecule Pt₃L₆ there are three filled metal-metal bonding MO's (e' + a₁') with a₁' being the HOMO. The LUMO is the metal-metal antibonding MO a₂' but just higher in energy are the three MO's derived from the empty 6p_z orbital on each Pt atom. The HOMO a₁' can be stabilized by interaction with an electrophile as shown in Figure 1 and, if the electrophile is the hypothetical CO²⁺ or H⁺, this will give rise to the clusters [Pt₃(μ ₃-CO)(μ -dppm)₃]²⁺ or [Pt₃(μ ₃-H)(μ -dppm)₃]⁺ respectively, both of which are stable complexes. The structure of the thiocyanate adduct of the carbonyl derivative is shown in Figure 2. One face of the Pt₃ triangle is blocked by the μ ₃-CO ligand but the other face is accessible and each platinum atom still has an empty 6p_z orbital available to add a ligand; in this a thiocyanate ligand is weakly coordinated. Some of the reactions with ligands, which can be considered to mimic chemisorption on a Pt(111) surface, are shown in Scheme 1⁶. These reactions convert the 42-electron cluster to 44, 46 or 48-electron clusters as one, two or three lone pairs of electrons from the incoming ligand are donated to the 6p_z orbital(s) on platinum and the reactions do not affect the metal-metal bonding in a significant way.