

# Hydrogen Sponge? A Heteronuclear Cluster That Absorbs Large Quantities of Hydrogen\*\*

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Clusters offer unique possibilities in reactivity that are not possible with mononuclear complexes, and different to that of nanoparticles and the bulk metallic state.<sup>[1]</sup> For example, while both mononuclear and cluster species can undergo ligand-substitution reactions by associative, dissociative, or intermediate mechanisms, ligand substitution in clusters can also be driven by metal–metal bond scission/reformation mechanisms (which in fact may be viewed as a special case of an associative reaction).<sup>[2]</sup> While activation by metal–metal bond scission could conceivably take place at the surface of a nanocluster, such a process would be very difficult to demonstrate experimentally. In contrast, clusters are soluble in common organic solvents and accordingly can be studied in solution by high-resolution spectroscopic techniques *in situ*.<sup>[3]</sup> Electronically unsaturated transition-metal carbonyl clusters open up further mechanistic possibilities, providing alternative mechanisms for ligand addition, substi-

tution, and C–X (and other) bond activation, which differ from those of clusters that obey the usual electron-counting rules, that is, the effective atomic number (EAN) rule and the polyhedral skeletal electron pair theory (PSEPT).<sup>[4]</sup>

A classic example of a low nuclearity (EAN) cluster that contains two electrons less than expected is  $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ . This cluster undergoes addition reactions with, for example, phosphines, to form clusters of formula  $[\text{Os}_3\text{H}_2(\text{CO})_{10}(\text{PR}_3)]$ . It can also undergo a more complicated addition/Si–H bond activation process with the functionalized phosphine  $\text{HMe}_2\text{SiC}_6\text{H}_4\text{CH}_2\text{PPh}_2$  to afford  $[\text{Os}_3\text{H}(\text{CO})_8(\text{Me}_2\text{SiC}_6\text{H}_4\text{CH}_2\text{PPh}_2)]$ .<sup>[5]</sup> In both reactions the resulting cluster core comprises a triangle in which all the Os–Os bond lengths are typical of single bonds.

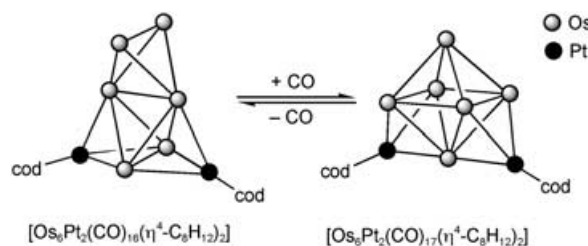
An interesting example of a high nuclearity cluster with two electrons less than the expected number is  $[\text{Os}_6\text{Pt}_2(\text{CO})_{16}(\eta^4\text{-C}_8\text{H}_{12})_2]$  (see Scheme 1).<sup>[6]</sup> The geometry can be described in various ways, but perhaps the simplest way to view the core is as four fused tetrahedra. The addition of two

electrons in the form of a CO ligand does not result in a simple transformation, instead a major structural rearrangement takes place, resulting in a cluster with a bicapped-octahedral core. Clusters with excessive electron counts are also known, for example,  $[\text{Ni}_6(\eta^5\text{-Cp})_6]$  (Cp =  $\text{C}_5\text{H}_5$ ) has an octahedral structure but has 90 electrons, four more than expected.<sup>[7]</sup>

The cationic tetrahedral platinum hydride clusters  $[\text{Pt}_4\text{H}_2(\text{PtBu}_3)_4]^{2+}$  and  $[\text{Pt}_4\text{H}(\text{PtBu}_3)_4]^+$  react rapidly with  $\text{H}_2$  to give the heptahydride cluster  $[\text{Pt}_4\text{H}_7(\text{PtBu}_3)_4]^{2+}$ , in which a Pt–Pt bond has been broken to afford a cluster with a butterfly geometry.<sup>[8]</sup> This process can be reversed by reaction with ethene.

Very recently Weller and co-workers reported a late-transition-metal cluster that is not just short of two electrons, but deficient by an electron count of 10 (though exactly comparable to the early-transition-metal cluster  $[\text{Nb}_6\text{Cl}_{18}]$ ).<sup>[9,10]</sup> The compound in question,  $[\text{Rh}_6(\mu\text{-H})_{12}(\text{P}i\text{Pr}_3)_6]^{2+}$ , has a regular octahedral geometry in which each vertex has a phosphine ligand and each edge is bridged by a hydride ligand. Now, Adams and Captain have discov-

ered an equally remarkable cluster,  $[\text{Pt}_3\text{Re}_2(\text{CO})_6(\text{PtBu}_3)_3]$  (1) that is also deficient by 10 electrons, but contains only five metal atoms—three platinum and two rhenium atoms.<sup>[11]</sup> The cluster was isolated from the reaction of  $[\text{Pt}(\text{PtBu}_3)_2]$  with  $[\text{Re}_2(\text{CO})_{10}]$  in refluxing octane in 18% yield. The trigonal bi-



**Scheme 1.** Polyhedral rearrangement observed on the formation of  $[\text{Os}_6\text{Pt}_2(\text{CO})_{17}(\eta^4\text{-C}_8\text{H}_{12})_2]$  from  $[\text{Os}_6\text{Pt}_2(\text{CO})_{16}(\eta^4\text{-C}_8\text{H}_{12})_2]$  following association of one CO ligand (cod =  $\text{C}_8\text{H}_{12}$ ; CO ligands omitted for clarity).

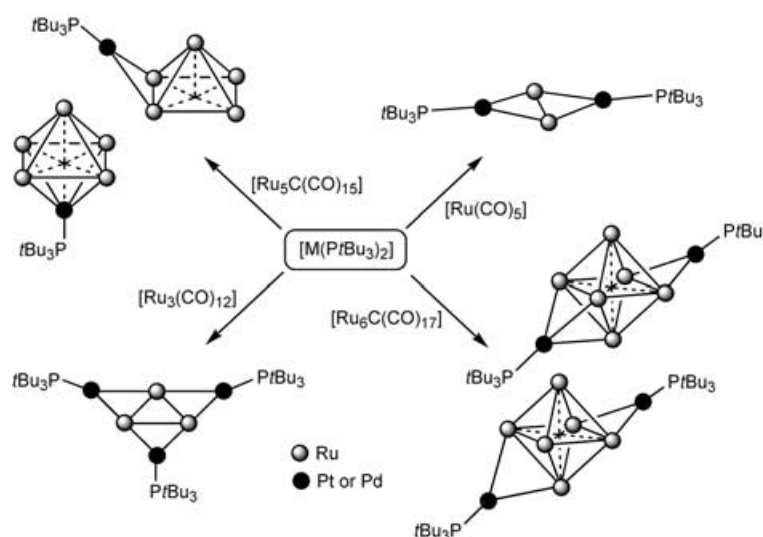
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[\*\*] We would like to thank Prof. Richard Adams for supplying the graphic used in the Table of Contents.

pyramidal geometry presented by this cluster is shown in Figure 1 a. The surface of the cluster is decorated with carbonyl and phosphine ligands and the space-filling diagram (Figure 1 b) reveals essentially complete encapsulation of the metal core by the ligand sphere.

In the presence of  $H_2$  at room temperature the cluster reacts to form  $[Pt_3Re_2(\mu-H)_6(CO)_6(PtBu_3)_3]$  (**2**). The cluster retains essentially the same geometry, including the original trigonal-bipyramidal core, and the crystal structure of **2** shows that all six of the Re–Pt bonds are bridged by hydride ligands. The hydride ligands were located in the high-quality X-ray structure, and significantly, the Pt–Re bond lengths had considerably lengthened (from an average of 2.648 in **1** to 2.909 Å in **2**).

The 14 valence-electron (VE) complex  $[Pt(PtBu_3)_2]$ , and the palladium analogue, have been used by Adams and co-workers to produce an array of fascinating new heteronuclear clusters, many with unusual electron counts. In their earlier work they described the reaction of  $[Pd(PtBu_3)_2]$  with  $[Ru_3(CO)_{12}]$  to afford the remarkable near-planar cluster  $[Ru_3(CO)_{12}\{Pd(PtBu_3)_3\}]_3$  (Scheme 2).<sup>[12]</sup> The utility of the reactive fragment was further demonstrated in the reaction with  $[Ru_6C(CO)_{17}]$  affording  $[Ru_6C(CO)_{17}\{Pd(PtBu_3)_2\}]_2$ , which exists as two isomers in the solid state, and with  $[Ru(CO)_5]$  yielding the complex  $[Ru_2(CO)_9\{Pd(PtBu_3)_2\}]_2$ , a dipalladium adduct of unstable  $[Ru_2(CO)_9]$ . Subsequently other compounds have been reported including  $[Ru_5C(CO)_{15}\{Pt(PtBu_3)_3\}]_2$ , which consists of two interconverting isomers in solution,<sup>[13]</sup> and



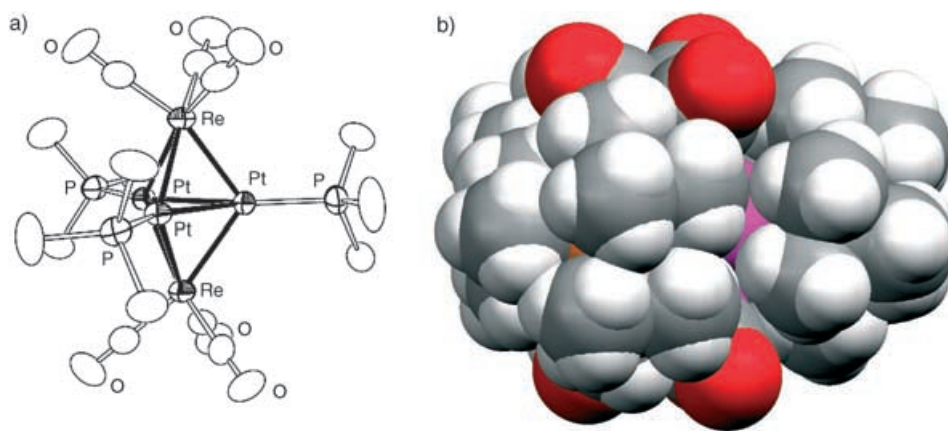
**Scheme 2.** Examples of condensation reactions between the highly reactive 14 VE complexes  $[M(PtBu_3)_2]$  ( $M = Pd$  or  $Pt$ ) and various ruthenium carbonyl compounds recently reported by Adams and co-workers (CO ligands omitted for clarity).

some rhodium–platinum,<sup>[14]</sup> and iridium–platinum<sup>[15]</sup> clusters containing up to 12 metal atoms.

Efficient hydrogen production and storage is of considerable importance in a world where cheap and renewable energy source are urgently needed, and although clusters are unlikely to be used for hydrogen storage, they should certainly serve as excellent models for this process. The replacement of nanoclusters in fuel cells by molecular clusters can also be envisaged and it is likely to be clusters such as  $[Pd_{28}(CO)_{27}(H_{12})\{Pt(PMe_3)\}\{Pt(PPh_3)\}_{12}]$ ,<sup>[16]</sup>  $[Pt_4H_8(PPh_2)_4]$ ,<sup>[17]</sup>  $[Rh_6(\mu-H)_{12}(PPr_3)_6]^{2+}$ , and  $[Pt_3Re_2(\mu-H)_6(CO)_6(PtBu_3)_3]$  that drive such possibilities forward. The heavy transition metals are of course

unlikely candidates for  $H_2$  storage by themselves, setting aside the fact that they are among the most rare and expensive of elements, to meet the US Department of Energy's recommendation for mobile applications of 6% hydrogen by weight,<sup>[18]</sup> each metal atom alone would have to reversibly absorb many hydrogen molecules. However, the rate and extent of adsorption of  $H_2$  on more promising substrates (light and cheap materials with high surface area, such as carbon) may be increased by using metal particles, which enhance hydrogen storage through hydrogen spillover.<sup>[19]</sup> Metal nanoparticles with a strong propensity for hydrogen absorption may prove to be useful models and/or precursors for this process. Furthermore, there will certainly be a demand for hydrogen storage beyond mobile applications.

Science follows trends, and not so long ago molecular clusters were in vogue, not just because of their fascinating structures, but also because of their potential to revolutionize catalysis and exhibit novel material properties. While the sheer quantity of publications in this area has certainly decreased from the heights of the late 1980s, fascinating new discoveries continue to be made. Notable synthetic develop-



**Figure 1.** The structure of **1**; a) ORTEP plot, b) space-filling model.

ments in cluster chemistry include the isolation of a nanosized, three-shelled spherical Pd<sub>145</sub> cluster;<sup>[20]</sup> giant polyoxomolybdate wheels,<sup>[21]</sup> a spectacular, protein-sized Mo<sub>368</sub> “nanohedgehog”,<sup>[22]</sup> and the exotic inorganic fullerenes [P<sub>60</sub>-(FeCp\*)<sub>12</sub>Cu<sub>25</sub>Cl<sub>25</sub>(MeCN)<sub>10</sub>]<sup>[23]</sup> (Cp\* = C<sub>5</sub>Me<sub>5</sub>) and [As@Ni<sub>12</sub>@As<sub>20</sub>]<sup>3-</sup>.<sup>[24]</sup> In addition, the employment of clusters as precursors to well defined supported nanoparticles has been elegantly demonstrated.<sup>[25]</sup> Indeed, part of the renaissance in molecular-cluster chemistry has been driven by the development of nanotechnology; the emphasis in this area of research is on objects whose size is between 0.1 to 100 nm, and the larger molecular clusters fit firmly into the lower end of this range. While nanotechnology is now in fashion, on a scale that molecular clusters never witnessed (metaphorically and in terms of absolute size), in many ways the aspirations remain the same, that is, catalysis, material science, but also in diagnostics and medicine. However, potential biomedical applications of clusters have also been recognized,<sup>[26]</sup> and it is not unreasonable to assume that as miniaturization continues, a natural regression in size may well mean that clusters fulfill their initial promise in an unexpected context.

It will certainly be interesting to see what Adams and Captain can do with their nascent discovery. The palladium analogue is an obvious target, given that the chemistry of [Pd(PrBu<sub>3</sub>)<sub>2</sub>] appears to parallel the platinum analogue. The ability of palladium metal to behave as a hydrogen sponge provides further impetus. The cluster **1** uptakes about 75 times its volume of H<sub>2</sub> (about 10% of the efficiency of palladium metal at a stoichiometry of PdH<sub>0.6</sub>, though much of this difference is due to the higher density of Pd—the % hydrogen by weight is 0.33% for **1** compared to 0.56% for PdH<sub>0.6</sub>), and finding a way of making this process reversible will be a key advance. The trigonal bipyramidal cluster **1** should be able to accommodate a further two equivalents of H<sub>2</sub> and still give a satisfactory electron count (and indeed, Adams and Captain found **1** has five low-lying unoccupied molecular

orbitals of which three are filled on formation of **2**). Whether the space is available for these four hydride ligands is less obvious—certainly three could occupy the remaining unbridged M–M edges, but the likely position of a fourth is not immediately clear. However, studies by Weller et al. have shown that octahedral rhodium clusters (12 M–M bonds) can possess up to 16 hydride ligands<sup>[27]</sup> so the possibility of having more hydrogen atoms than edges is certainly feasible. Clusters rich in hydrogen with both terminal and bridging hydride ligands are also known.<sup>[17]</sup> In such cases, neutron diffraction studies to discern the exact locations of the hydride ligands are desirable. Many questions can be asked about the chemistry of a cluster as unsaturated as **1**. For example, is the oxidative addition of substrates other than hydrogen possible? It is possible to imagine, for example, the oxidative addition or association of different substrates onto the cluster framework followed by recombination in new and different ways to those possible with existing systems.

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