Cluster Compounds

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. [1] 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).[2]

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.[3] Electronically unsaturated transition-metal carbonyl clusters open up further mechanistic possibilities, providing alternative mechanisms for ligand addition, substitution, 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).[4]

A classic example of a low nuclearity (EAN) cluster that contains two electrons less than expected is [Os6H2(CO)10]. This cluster undergoes addition reactions with, for example, phosphines, to form clusters of formula [Os6H2(CO)10(PR3)]. It can also undergo a more complicated addition/Si–H bond activation process with the functionalized phosphine HMe2SiC6H4CH2PPh2 to afford [Os6(H2CO)(Cp6)Pr3].[5] 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 expected is [Os3H2(CO)10]. This cluster contains two electrons less than expected.

Clusters with excessive electron counts are also known, for example, [Ni6((η5-C5H5)6)], which has 90 electrons, four more than expected.[7]

The cationic tetrahedral platinum hydride clusters [Pt4H(PBu3)4]+ and [Pt4H2(PBu3)2]3+ react rapidly with H2 to give the heptahydride cluster [Pt4H7(PBu3)3]4+, in which a Pt–Pt bond has been broken to afford a cluster with a butterfly geometry.[8] 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 [Nb10C18]2−).[9] The compound in question, [Rh14(μ-H)26(PPr3)2]4+, 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 discovered an equally remarkable cluster, [Pt4Re2(CO)8(PBu3)2] (1) that is also deficient by 10 electrons, but contains only five metal atoms—three platinum and two rhenium atoms.[10] The cluster was isolated from the reaction of [Pt(PBu3)]4 with [Re2(CO)10] in refluxing octane in 18% yield. The trigonal bi-
pyramidal geometry presented by this cluster is shown in Figure 1a. The surface of the cluster is decorated with carbonyl and phosphine ligands and the space-filling diagram (Figure 1b) 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$_3$Re$_2$(μ-H)$_6$(CO)$_6$(PtBu)$_3$]$_2$ (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 Å in 1 to 2.909 Å in 2).

The 14 valence-electron (VE) complex [Pt(PtBu)$_3$], 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)$_3$] with [Ru$_5$(CO)$_{12}$] to afford the remarkable near-planar cluster [Ru$_5$(CO)$_{12}$Pd(PtBu)$_3$] (Scheme 2).[12] The utility of the reactive fragment was further demonstrated in the reaction with [Ru$_5$(CO)$_{12}$] affording [Ru$_5$(CO)$_{12}$Pd(PtBu)$_3$], which exists as two isomers in the solid state, and with [Ru$(CO)_3$] affording the complex [Ru$_4$(CO)$_{12}$Pd$(PtBu)_3$], which consists of two inter-converting isomers in solution, and some rhodium–platinum, and iridium–platinum 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$_n$(CO)$_{2n}$] and [Pt$_n$(CO)$_{2n}$] 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,[18] 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.[19] 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-
In the context of cluster chemistry, the employment of clusters as precursors to well-defined supported nanoparticles has been elegantly demonstrated. Indeed, part of the renaissance in molecular-cluster chemistry has been recognized, and it is not unreasonable to assume that as miniaturization continues, a natural regression in size may well mean that clusters fulfill the role of hydrogen sponges. The platinum analogue is an obvious target, given what Adams and Captain can do with palladium metal at a pressure of 1 atmosphere. It will certainly be interesting to see what Adams and Captain can do with palladium metal at a pressure of 1 atmosphere.

Highlights