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Hydrogen Storage

Hydrogen Activation by Unsaturated Mixed-Metal Cluster Complexes: New Directions

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cluster compounds · H–H activation · hydrogen · hydrogenation

In memory of F. Albert Cotton

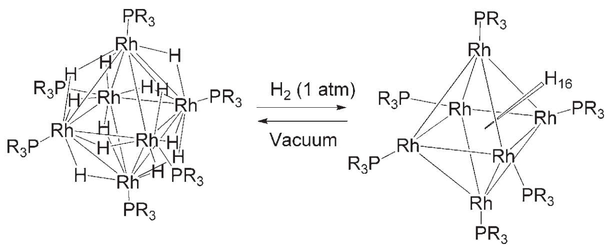
There has been a renewed interest in the chemistry of hydrogen as a result of the ever-increasing global demands for energy. Recent studies have revealed new electronically unsaturated polynuclear metal complexes containing bulky ligands that exhibit a variety of reactions with hydrogen, including facile addition and elimination under mild conditions. Materials and molecules that can reversibly absorb large quantities of hydrogen are very attractive for hydrogen storage and hydrogenation catalysis. This Minireview summarizes recent studies of reactions of hydrogen with unsaturated mixed-metal cluster complexes containing platinum and bulky phosphine ligands. Some related studies on bimetallic cooperativity and the synthesis of trimetallic nanoparticles on mesoporous supports that exhibit high activity and selectivity for catalytic hydrogenations are also discussed.

1. Introduction

Hydrogen is and will continue for the foreseeable future to be one of the most important elements for chemists and the chemical industry. The storage and utilization of hydrogen will be central to any plans for the development of a "hydrogen economy".[1] The safe and efficient utilization of hydrogen for energy-related purposes is going to require catalysts.[2] The activation of hydrogen by metals is a fundamental step in nearly all catalytic hydrogenation reactions.[3]

Over the years, hydrogen-rich polynuclear metal complexes have captured the attention of cluster chemists. There are a number of reported examples in which mononuclear metal complexes are condensed under the influence of hydrogen to form high nuclearity complexes containing large number of hydride ligands, for example, $[Rh_6(PR_3)_6H_{12}][BAr^F_4]_2$ (R = iPr, Cy; $BAr^F_4 = [B\{C_6H_3(CF_3)_2\}_4]$),[4a] $[H_8Cu_8(Ph_2P(CH_2)_3PPh_2)_4]$,[4b] $[Pt_5(PtBu_2Ph)_5H_8]$,[4c] $[Pt_4H_8(PiPr_2Ph)_4]$,[4d] and $[\{Ir_3H_6(PR_3)_3py_3\}(\mu_3\text{-}H)](PF_6)_2$ (R = Cy or iPr).[4e] Interestingly, $[Rh_6(PR_3)_6H_{12}][BAr^F_4]_2$ is also capable of adding two equivalents of hydrogen reversibly under very mild conditions (Scheme 1).

Süss-Fink et al. have shown that the unsaturated tetraruthenium cationic complex $[Ru_4(C_6H_6)_4H_4]^{2+}$ adds one equivalent of H_2 at 59 atm and 55 °C to form the hexahydrido complex $[Ru_4(C_6H_6)_4H_6]^{2+}$, which contains a bridging H_2 ligand.[5]



Scheme 1.

2. Unsaturated Mixed-Metal Clusters for Hydrogen Activation

Most of the compounds mentioned in the Introduction contain bulky phosphine ligands. It is well established that highly sterically crowded ligands can provide stable, electronically unsaturated metal complexes by preventing the other ligands from entering the coordination sphere of the metal atom. It is precisely this effect that led to the formation

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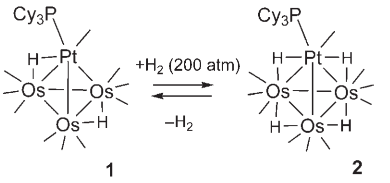
of the first molecular-hydrogen metal complexes.[6] In the remainder of this Minireview, we will concentrate on the chemistry of unsaturated mixed-metal cluster complexes for hydrogen activation and for its implications for catalytic hydrogenation reactions.[7]

In early work, Stone and co-workers showed that the unsaturated 58-electron complex [$PtOs_3(CO)_{10}(PCy_3)(\mu\text{-}H)_2$] (**1**) adds hydrogen reversibly to yield the tetrahydrido complex [$PtOs_3(CO)_{10}(PCy_3)(\mu\text{-}H)_4$] (**2**), but the addition reaction requires a pressure of 200 atm H_2 [Eq. (1); terminal CO ligands here and following represented by −].[8] When the H_2 pressure is released, compound **2** is converted back into **1**. This would be an attractive system for hydrogen storage if it were not based on high-molecular-weight materials of precious metals.



(1)

In recent studies we have shown that stable, highly unsaturated mixed-metal cluster complexes can be prepared by the reactions of [$Pt(PtBu_3)_2$] with selected polynuclear metal carbonyl cluster complexes. For example, the reaction of [$Pt(PtBu_3)_2$] with [$Re_2(CO)_{10}$] yielded the highly unsaturated heterometallic complex [$Pt_3Re_2(CO)_6(PtBu_3)_3$] (**3**).[9] The structure of compound **3** consists of a trigonal-bipyramidal cluster of five metal atoms: three of platinum and two of rhenium. {$Re(CO)_3$} groups occupy the two apical positions of the cluster. The three Pt atoms define the equatorial plane, and each platinum atom contains one large $PtBu_3$ ligand. Compound **3** has only 62 valence electrons. This is 10 electrons less than the number expected for a trigonal bipyramidal cluster of five metal atoms.[10] Molecular orbital calculations have revealed the presence of five low-lying molecular orbitals on the metal atoms that can accommodate the 10 missing electrons.

Most interestingly, we have found that not only does this complex sequentially add three equivalents of hydrogen to yield a series of three hydride-containing compounds—the dihydrido, tetrahydrido, and hexahydrido complexes [$Pt_3Re_2(CO)_6(PtBu_3)_3(\mu\text{-}H)_2$] (**4**), [$Pt_3Re_2(CO)_6(PtBu_3)_3(\mu\text{-}H)_4$] (**5**), and [$Pt_3Re_2(CO)_6(PtBu_3)_3(\mu\text{-}H)_6$] (**6**), respectively (Figure 1)—but it also undergoes this addition process at room temperature. The hydrido ligands were shown to bridge the Pt−Re bonds of the cluster in each of the compounds. Even more interestingly, up to four of the hydrido ligands in **6** can be expelled by the application of UV/Vis irradiation; that is, the hexahydrido complex **6** expels one and two equivalents of hydrogen to regenerate the tetrahydrido and dihydrido complexes **5** and **4**, respectively.[9a] Experimental evidence has indicated that the hydrogen addition sequence proceeds without the elimination of an existing ligand; that is, generation of a so-called "vacant" site appears not to be a part of the hydrogen addition mechanism. Space-filling models of compound **3** show that there is enough room for an H_2 molecule to penetrate the coordination sphere without

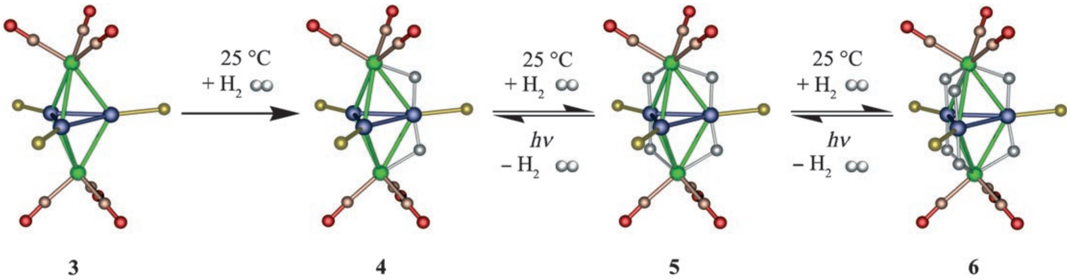


Figure 1. Reversible addition of H_2 to the {Pt_3Re_2} cluster complex **3**. Blue Pt, green Rh, yellow P, red O, light brown C, gray H.

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the loss of one of the existing ligands (Figure 2). The platinum atoms in **3** can actually be seen (shown in blue) in Figure 2.

Possible mechanisms for the addition of H_2 to **3** have been investigated by computational methods.[9a] After penetrating the ligand sphere, the hydrogen molecule most likely adds initially to a single metal atom. Early theoretical considerations have shown that the concerted four-center addition/elimination of H_2 to/from two metal atoms in an orientation parallel to a metal–metal bond is an orbitally forbidden process and is energetically unfavorable.[11] Two possibilities for hydrogen addition to **3** at a single metal site have been considered, one at platinum and one at rhenium. Energetically, addition at each metal atom is reasonable, but the addition and activation at a platinum atom is slightly more favorable than the addition at rhenium. Figure 3 depicts the nature of the hydrogen addition and the cleavage of the H−H bond at a platinum site. Initially, the hydrogen molecule adds in the established η^2 mode (see Figure 3a).[6] After addition, the H_2 ligand then shifts toward one of the neighboring platinum atoms in the equatorial plane. The H−H bond length increases and the bond then breaks (Figure 3b). One of the hydrogen atoms then becomes a bridging hydrido ligand across a Pt−Pt bond, and the other hydrogen atom becomes a terminal hydrido ligand on the platinum atom to which the H_2 molecule was originally added (Figure 3c). The series of steps strongly indicates that the H−H bond cleavage is assisted by the interactions of the H_2 ligand with the neighboring platinum atom. This may be a characteristic and beneficial feature for hydrogen activation in unsaturated polynuclear metal complexes in general.

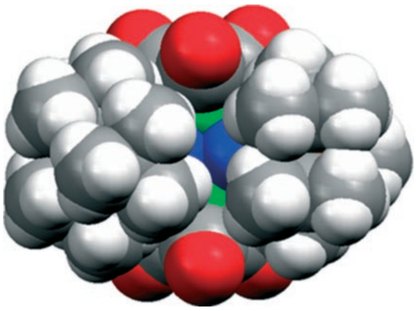


Figure 2. Space-filling model of **3** showing a channel between the ligands to the metal atoms. Blue Pt, green Rh, red O, gray C, white H.

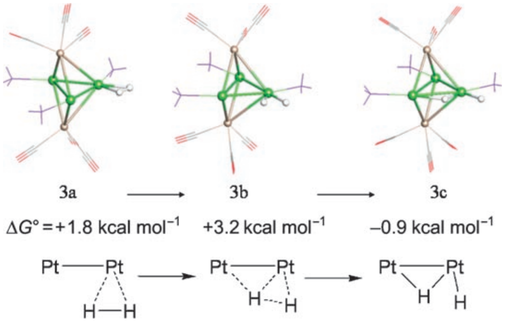


Figure 3. Calculated structures **3a–c** showing a possible mode of activation of H_2 by platinum in the compound $[Pt_3Re_2(CO)_6(PtBu_3)_3]$ (**3**). Green Pt, beige Rh, white H.

Another very interesting highly unsaturated mixed-metal cluster complex is the 54-electron platinum–rhenium complex $[Pt_2Re_2(CO)_7(PtBu_3)_2(\mu\text{-}H)_2]$ (**7**), which we recently obtained from the reaction of $[Pt(PtBu_3)_2]$ with $[PtRe_2(CO)_9(PtBu_3)(\mu\text{-}H)_2]$.[12] Electronically saturated tetrahedral four-metal cluster complexes should contain 60 valence electrons.[10] Complex **7** also adds hydrogen at room temperature and 1 atm H_2, but, unlike the reaction of **3**, only one equivalent of H_2 is added to **7** to yield the 56-electron tetrahydrido cluster complex $[Pt_2Re_2(CO)_7(PtBu_3)_2(\mu\text{-}H)_4]$ (**8**, Figure 4), once again without any evidence of ligand loss. Most importantly, the addition of H_2 to **7** is fully reversible. When heated to 97 °C or irradiated (UV/Vis) at 25 °C, **8** loses one equivalent of hydrogen to regenerate **7** in high yield. The platinum atoms in **7** are significantly different. One contains one phosphine ligand and one CO ligand, whereas the other has one phosphine ligand but no CO ligand. Not surprisingly then, a computational investigation of the mechanism of hydrogen activation by **7** suggested that the hydrogen molecule was added and activated at the platinum atom that does not have the CO ligand.

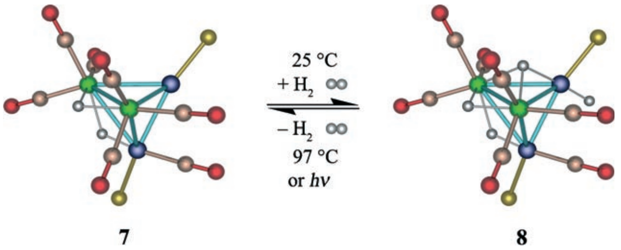


Figure 4. Reversible addition of hydrogen to the $\{Pt_2Re_2\}$ cluster complex **7**. Color code: see Figure 1.

Recently, we also prepared the 68-electron heteronuclear five-metal cluster complex $[Pt_2Os_3(CO)_{10}(PtBu_3)_2]$ (**9**).[13] This complex was obtained from the reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with $[Pt(PtBu_3)_2]$. This molecule contains a trigonal-bipyramidal cluster of five metal atoms, but, unlike compound **3**, in **9** the platinum atoms occupy the axial sites and a triangle of osmium atoms defines the equatorial plane (Figure 5). This complex is also electron-deficient, but in this case only by four electrons. Nevertheless, it does sequentially add two equivalents of hydrogen reversibly to form the di- and tetrahydrido cluster complexes $[Pt_2Os_3(CO)_{10}(PtBu_3)_2(\mu\text{-}H)_2]$ (**10**) and $[Pt_2Os_3(CO)_{10}(PtBu_3)_2(\mu\text{-}H)_4]$ (**11**), and this hydrogen addition proceeds smoothly even at 0 °C. Unlike the addition of hydrogen to **3** and **7**, the addition of hydrogen to **9** involves the cleavage of a metal–metal bond, a platinum–osmium bond, in particular. Thus, the structure of **10** consists of a tetrahedral $\{Os_3Pt\}$ cluster with a $\{Pt(PtBu_3)\}$ group bridging an Os−Os edge of the $\{Os_3Pt\}$ cluster. Compound **11** contains an $\{Os_3\}$ triangle with two edge-bridging $\{Pt(PtBu_3)(CO)\}$ groups formed by the cleavage of two Pt−Os

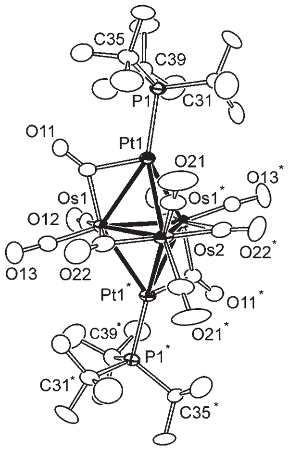
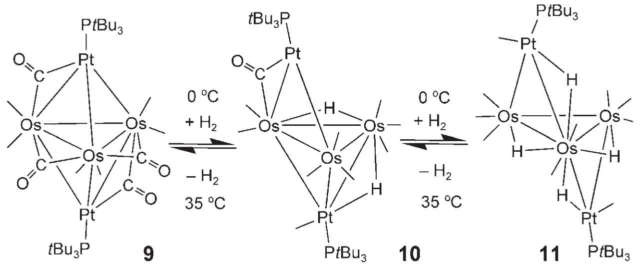


Figure 5. The molecular structure of **9**.

bonds. When **10** and **11** are heated, hydrogen is eliminated in the form of H_2 and the cluster closes again to form **9** (Scheme 2). Although this hydrogen-addition process is facile, the cleavage of some of the metal–metal bonds renders the clusters of the product complexes less stable and these complexes degrade much more easily than those of the hydride-containing platinum–rhenium complexes **4**–**6** described above that are formed by hydrogen-addition processes that do not involve metal–metal bond-cleavage processes.

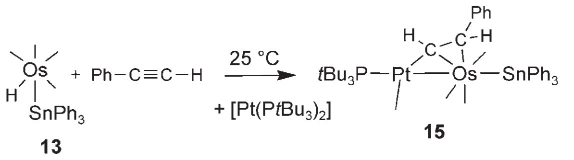


Scheme 2.

3. Platinum Activation of Metal–Hydrogen Bonds for Alkyne Insertion Reactions

We have also shown that the {Pt(P*t*Bu$_3$)} group can activate metal–hydride bonds in complexes toward alkyne-insertion reactions. The insertion of unsaturated hydrocarbons into the metal–hydrogen bond is an integral part of the process of catalytic hydrogenation reactions.[3a]

We have prepared the tin-containing metal–hydride complexes [HM(CO)$_4$SnPh$_3$] (M = Ru (**12**) and Os (**13**)).[14] These complexes have 18-electron configurations and thus do not react with alkynes such as PhC$_2$H under mild conditions. However, in the presence of [Pt(P*t*Bu$_3$)$_2$], there is a rapid reaction of **12** and **13** with PhC$_2$H at room temperature to yield the bimetallic complexes [PtM(CO)$_4$(SnPh$_3$)(P*t*Bu$_3$){μ-HC$_2$(H)Ph}] [M = Ru (**14**) and Os (**15**), Eq. (2)].[14]



(2)

The molecular structure of **15** (Figure 6) reveals a bimetallic complex with a phenylalkenyl (HC$_2$(H)Ph) ligand bridging a Pt–Os bond. The HC$_2$(H)Ph ligand was formed by the insertion of the PhC$_2$H into the Os–H bond with transfer of the hydrogen atom to the phenyl-substituted carbon atom of the alkyne. The phenylalkenyl ligand has *E* stereochemistry, which is consistent with *cis* insertion of the alkyne into the metal–hydrogen bond via the classical four-center transition state.

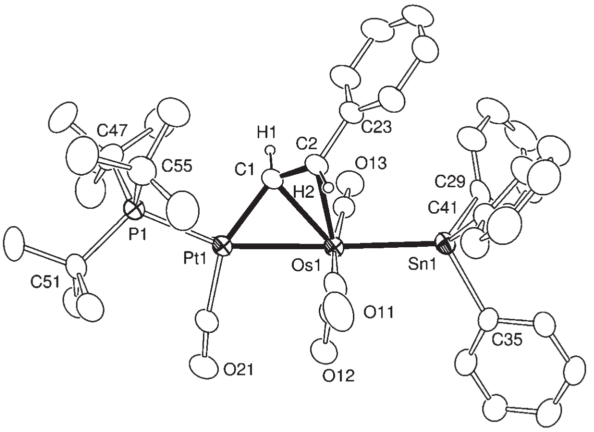


Figure 6. The molecular structure of **15**.

To try to understand the nature of the activation of the Os–H bond by the {Pt(P*t*Bu$_3$)} group, we examined the reaction of **13** with [Pt(P*t*Bu$_3$)$_2$] in the absence of PhC$_2$H. From this reaction we isolated the complex [PtOs(CO)$_4$(SnPh$_3$)(P*t*Bu$_3$)(μ-H)] (**16**, Figure 7). The structure of **16** shows that a {Pt(P*t*Bu$_3$)} group was added to the osmium atom. A Pt–Os bond was formed and the hydrido ligand and one CO group became bridging ligands across that Pt–Os bond. When phenylacetylene was added to **16**, compound **15** was formed in high yield, which demonstrates that complex **16** is an intermediate in the formation of **15** by Equation (2). The structure of **16** shows that the {Pt(P*t*Bu$_3$)} group activates the Os–H bond by forming a bonding interaction both to the metal atom and the hydrido ligand. The Os–H bond in **16** is 0.20 Å longer and presumably weaker than that in **13**.

Complex **16** is also electronically unsaturated. It contains only 30 valence electrons between the two metal atoms. By using molecular orbital calculations, we examined the electronic structure of **16** and found a low-lying empty atomic orbital on the platinum atom which appears to play a key role

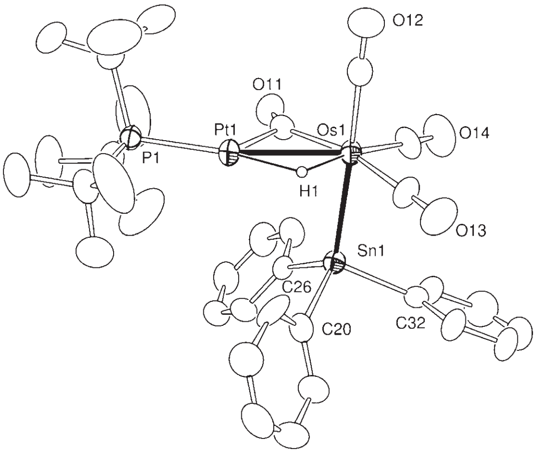


Figure 7. The molecular structure of **16**.

in facilitating the addition of the phenylacetylene molecule to the complex by providing a low-energy pathway for its initial coordination. The lowest unoccupied molecular orbital (LUMO) of **16** (Figure 8) contains an empty d-orbital component on the platinum atom that is shown on the left. A proposed mechanism for the platinum-assisted addition and insertion of PhC_2H to **13** is shown in Scheme 3. The C–C triple bond of the PhC_2H molecule is added to the platinum atom, which then facilitates the formation of a bonding interaction between the phenyl-substituted carbon atom and the bridging hydrido ligand. A $HC_2(H)Ph$ ligand is then formed which may initially be π-coordinated to the platinum center (for example, proposed intermediate **A**), which then isomerizes to the final product **15**. This binuclear cooperativity or synergism, as shown by the reaction of **16** with PhC_2H, may be a general phenomenon that could play an important role in many types of activation processes that are fundamental to homogeneous catalysis.

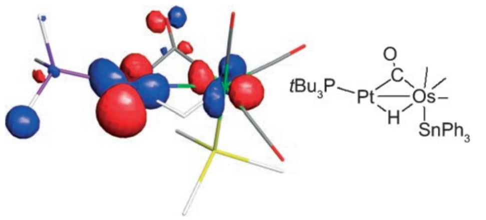
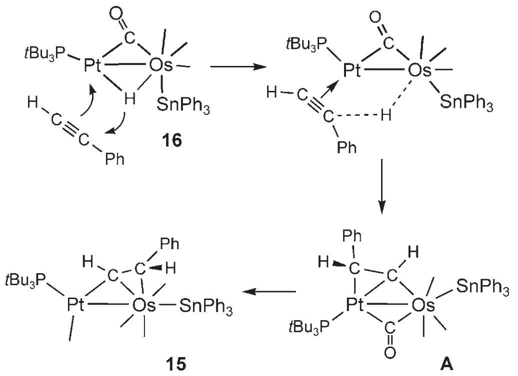


Figure 8. LUMO of **16**.



Scheme 3.

4. Toward New Supported Heterogeneous Mixed-Metallic Nanocatalysts

In recent collaborations with J. M. Thomas and R. Raja, we have shown that our mixed-metal cluster complexes containing platinum, ruthenium, and tin can provide heterogeneous nanoparticle hydrogenation catalysts with exceptionally high activity and selectivity when they are deposited on mesoporous supports and thermally activated to remove their ligands.[15] When the ligands are removed, the metal nanoparticles become highly unsaturated electronically and exhibit high reactivities both to hydrogen and to selected substrates. The sterically crowded phosphine ligands are not required for these catalysts to function. Instead, the clusters are stabilized by the silica supports. We believe that the tin also helps to stabilize high dispersions of the catalyst particles.[15–17] This stabilization may be attributed to the oxophilic character of tin that helps to bind the metal particles to the oxygen atoms of the support.

In preliminary studies, we demonstrated the superior catalytic properties of a heterometallic nanocatalyst formed by using the trimetallic cluster complex $[PtRu_5(SnPh_2)(CO)_{15}(\mu_6\text{-}C)]$ as a catalyst precursor. From this precursor, we prepared the trimetallic catalyst $PtSnRu_5$ as 1–2-nm particles on a mesoporous silica support (Figure 9).[15]

These trimetallic nanoparticles were found to be excellent catalysts for the single-step hydrogenation of dimethylterephthalate (DMT) to cyclohexanedimethanol (CHDM) at

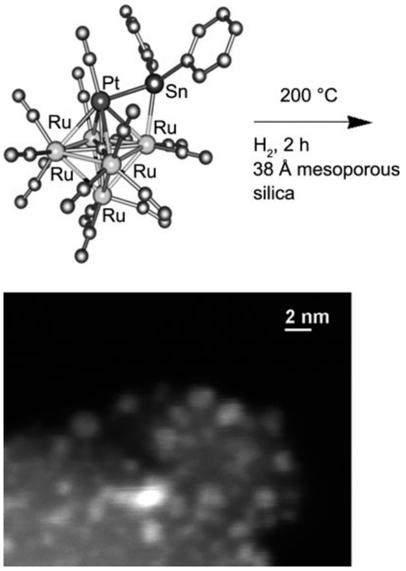
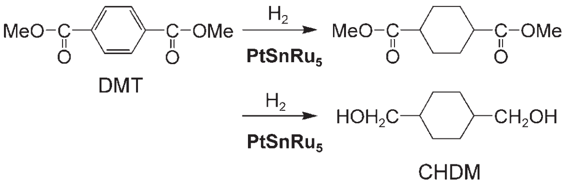


Figure 9. Activation of trimetallic $[PtRu_5(SnPh_2)(CO)_{15}(\mu_6\text{-}C)]$ cluster on mesoporous silica yields trimetallic $PtRu_5Sn$ nanoparticles.

100 °C and 20 atm H_2.[15] This is a very difficult reaction, and our catalyst is the most active catalyst for it reported to date [Eq. (3)].



(3)

CHDM is used on large scales by the chemical industry to make valuable copolymers when it is combined with DMT.[18] This new nanoscale catalyst has precisely the same stoichiometric metal composition as the precursor complex and it remains in a highly dispersed form throughout the course of the catalytic reaction. One of the most important features of this catalyst is that it reduces unsaturated oxygenate functional groups without cleaving C–O bonds. This feature is most important when products containing OH functional groups are desired.

5. Summary

We have shown that introducing {Pt(P*t*Bu$_3$)} groups into polynuclear metal carbonyl cluster complexes can provide highly unsaturated mixed-metal cluster complexes that can activate hydrogen reversibly under mild conditions. There is evidence that the {Pt(P*t*Bu$_3$)} group can also activate metal–hydrogen bonds in metal–hydride complexes. In addition, the intimate mixing of different metals provided by these mixed-metal precursor complexes gives improved control over metal composition and may pave the way to a new generation of mixed-metal heterogeneous catalysts on mesoporous supports.[15]

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