Facile Activation of Hydrogen by an Unsaturated Platinum−Osmium Cluster Complex

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The activation of hydrogen under mild conditions is an important first step in catalytic hydrogenation reactions.[1] Catalysts will play key roles in future applications of hydrogen as a fuel.[2] Hydrogen activation may even be valuable in the design and efficient use of hydrogen storage systems. There are active searches for molecules and materials that can reversibly absorb large amounts of hydrogen.[3,4] Recent studies have shown that unsaturated polynuclear metal complexes containing of bulky phosphine ligands can absorb relatively large amounts of hydrogen under mild conditions,[5-7] but there are only a few examples of thermally reversible hydrogen additions to polynuclear metal complexes that are not accompanied by the addition and elimination of other ligands.[6-9] A very interesting family of these compounds are the hexarhodium complexes, $[Rh_6(PR_3)_6H_{12}][BAr^F_4]_2$, R = ^iPr, Cy; Ar^F = $[B\{C_6H_3-(CF_3)_2\}_4]$, that were recently reported by Weller and co-workers.[6] These complexes add two more equivalents of hydrogen, reversibly, to yield the hexadecahydride complexes $[Rh_6(PR_3)_6H_{16}][BAr^F_4]_2$, R = ^iPr, Cy; Ar^F = $[B\{C_6H_3(CF_3)_2\}_4]$.

In recent studies we have shown that it is possible to prepare electronically unsaturated *bi*-metallic cluster complexes that are able to add significant amounts of hydrogen under mild conditions, e.g., 25 °C.[7,9] For example, the 62-electron cluster complex $Pt_3Re_2(CO)_6(P^tBu_3)_3$, **1** adds three equivalents of hydrogen at room temperature to yield the hexahydrido complex $Pt_3Re_2(CO)_6(P^tBu_3)_3(\mu-H)_6$, **2**, as shown in Scheme 1.[7]

Scheme 1
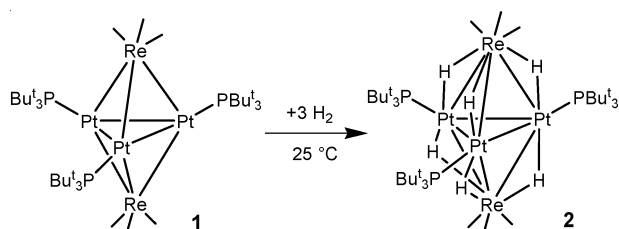
We have now prepared the new unsaturated pentanuclear platinum−osmium cluster complex, $Pt_2Os_3(CO)_{10}(P^tBu_3)_2$, **3**, that sequentially adds two equivalents of hydrogen at 0 °C by a series of metal framework cluster opening transformations that are also partially reversible. The reaction of $Os_3(CO)_{10}(NCMe)_2$ with $Pt-(P^tBu_3)_2$ at 0 °C has provided **3** in 20% yield. The five metal atoms in **3** were shown by an X-ray crystallographic analysis to have a trigonal bipyramidal structure with the three osmium atoms in the trigonal plane and the two platinum atoms in the axial positions, see Figure 1 (Left). The molecule lies on a crystallographic two-fold rotational axis that passes through atom Os(2). Each platinum atom contains one P^tBu_3 ligand. Compound **3** contains 68 cluster valence electrons, four less than the 72 electrons expected for a trigonal bipyramidal cluster in which all metal atoms have 18 electron configurations.[10] The 68-electron count can be explained
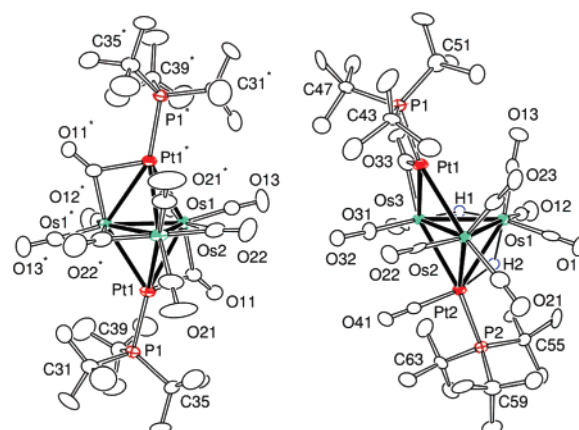

Figure 1. (Left) ORTEP diagram of $Pt_2Os_3(CO)_{10}(P^tBu_3)_2$, **3**, showing 30% probability thermal ellipsoids. Selected bond distances (Å) are as follows: Os(1)−Os(1*) = 2.8590(6), Os(1)−Os(2) = 2.7024(5), Pt(1)−Os(1) = 2.7923(3), Pt(1)−Os(1*) = 2.8104(4), Pt(1)−Os(2) = 2.8840(4), Pt(1)−P(1) = 2.3426(18). (Right) ORTEP diagram of $Pt_2Os_3(CO)_{10}(P^tBu_3)_2(\mu-H)_2$, **4**, showing 70% probability thermal ellipsoids. Selected bond distances (Å) are as follows: Os(1)−Os(2) = 2.7757(6), Os(1)−Os(3) = 2.9217(6), Os(2)−Os(3) = 2.7104(6), Pt(1)−Os(2) = 2.8339(6), Pt(1)−Os(3) = 2.7352(6), Pt(2)−Os(1) = 2.8821(6), Pt(2)−Os(2) = 2.8350(7), Pt(2)−Os(3) = 2.8093(6), Pt(1)−P(1) = 2.298(3), Pt(2)−P(2) = 2.402(3).

by assuming that the two platinum atoms have 16-electron configurations.

When compound **3** was exposed to hydrogen (1 atm) at 0 °C in methylene chloride solution, the dihydrido complex $Pt_2Os_3(CO)_{10}(P^tBu_3)_2(\mu-H)_2$, **4**, was formed in 93% yield within 10 min. The molecular structure of **4** was established crystallographically and is shown in Figure 1 (Right). The molecule contains five metal atoms with a platinum atom bridging an Os−Os edge of tetrahedral $PtOs_3$ cluster. The cluster was formed by cleaving one of the Pt−Os bonds in the cluster of **3**. The hydrido ligands were determined to occupy positions bridging the Os(1)−Os(3) and Os(1)−Pt(2) metal−metal bonds by a combination of the X-ray diffraction measurements and ^1H NMR spectroscopy which shows two resonances with suitable $^1H-^{195}Pt$ and $^1H-^{31}P$ couplings: $\delta = -10.49$, $^1J_{Pt}-H = 559$ Hz, $^3J_P-H = 11$ Hz and $\delta = -10.71$, $^2J_{Pt}-H = 23$ Hz, $^2J_{Pt}-H = 25$ Hz. Compound **4** has a total of 70 valance electrons. This is four electrons less than what would be expected for such a structure with all metal atoms having 18 electron configurations.[10] As with **3**, this deficiency can be explained by assuming that the two platinum atoms have 16-electron configurations.

When solutions of **4** in methylene chloride solvent were exposed to hydrogen at 1 atm at 0 °C for 1 h, the tetrahydrido complex $Pt_2Os_3(CO)_{10}(P^tBu_3)_2(\mu-H)_4$, **5**, was formed in 70% yield. Compound **5** can be also obtained directly from **3** in 63% yield by similar treatment.
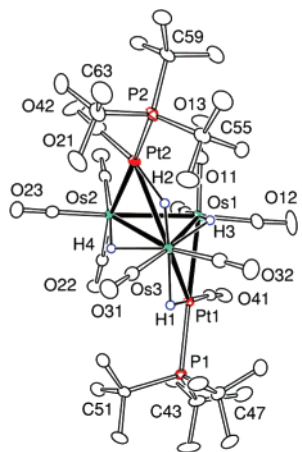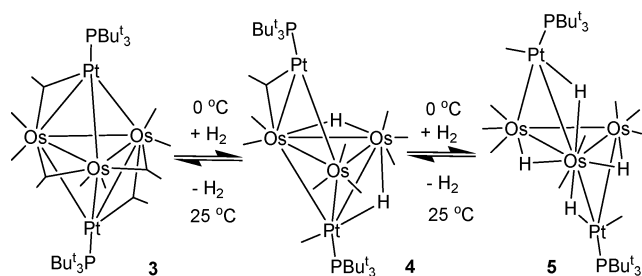
Figure 2. ORTEP diagram of $Pt_2Os_3(CO)_{10}(P^tBu_3)_2(\mu\text{-}H)_4$, **5**, showing 30% probability thermal ellipsoids. Selected bond distances (Å) are as follows: Os(1)−Os(2) = 2.8590(2), Os(1)−Os(3) = 2.9349(2), Os(2)−Os(3) = 2.9197(2), Pt(1)−Os(1) = 2.7670(2), Pt(1)−Os(3) = 2.8831(2), Pt(2)−Os(2) = 2.7580(2), Pt(2)−Os(3) = 2.8854(2), Pt(1)−P(1) = 2.3746(10), Pt(2)−P(2) = 2.3835(10), Pt(1)−H(1) = 1.80(6), Pt(2)−H(2) = 1.78(6), Os(1)−H(3) = 1.67(5), Os(2)−H(4) = 1.55(5), Os(3)−H(1) = 1.85(6), Os-(3)−H(2) = 1.61(6), Os(3)−H(3) = 1.82(5), Os(3)−H(4) = 1.98(5).

Scheme 2

The structure of **5** was shown crystallographically to contain a triangular Os₃ cluster with two *edge*-bridging Pt(CO)(PᵗBu₃) groups, see Figure 2. The four hydrido ligands were located and refined crystallographically. Their locations are supported by the ¹H NMR spectra.[11] All four hydrido ligands bridge metal−metal bonds to atom Os(3). One hydrido ligand bridges to each platinum atom while the other two bridge Os−Os bonds. Compound **5** has a total of 72 valance electrons which is four electrons less than is expected for such a structure with all metal atoms having 18-electron configurations.

Most interestingly, we have found that the facile hydrogen additions to **3** and **4** are partially reversible. When nitrogen is purged through a solution of **5** in benzene at 25 °C for 10 h, compounds **3** and **4** were formed and isolated in the yields 22% and 33%, respectively; 28% of the original amount of **5** was recovered. When **5** was dissolved in CD₂Cl₂ and heated to 35 °C for 1 h in a sealed NMR tube, the formation of hydrogen was observed at 4.60 ppm by ¹H NMR spectroscopy.

A schematic of the hydrogen addition/cluster transformation reactions reported here are shown in Scheme 2. With each addition of hydrogen, a Pt−Os bond to one of the Pt(PᵗBu₃) capping groups is cleaved.

To help to understand the electronic structure of **3** and the nature of the hydrogen addition process, we have performed Fenske− Hall molecular orbital calculations. A contour diagram of the LUMO in **3** is shown in Figure 3. It can be seen that this empty orbital is concentrated on the platinum atoms but extends to a neighboring Pt−Os bond. This would be consistent with the

hydrogen addition at a platinum atom accompanied by cleavage of the associated Pt−Os bonds as observed. Further studies are in progress.
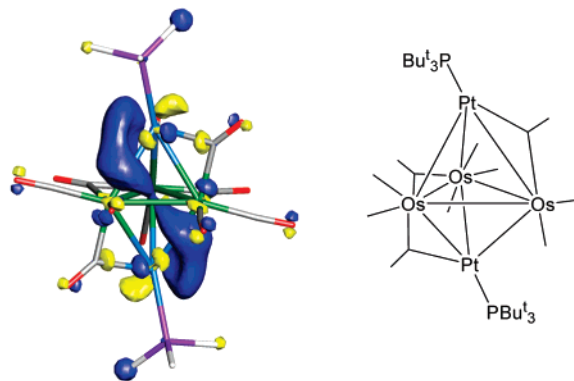

Figure 3. Contour diagram of the lowest unoccupied molecular orbital LUMO of **3** shows it is concentrated on the platinum atoms and extends to adjacent Pt−Os bonds.

Supporting Information Available: Crystallographic data of **3**−**5** in CIF format and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) For **5**, ¹H NMR (in CDCl₃): δ = 1.52 (d, 54H, CH₃, ³J_{P−H} = 13 Hz), −9.01 (m, 1H, hydride, ¹J_{Pt−H} = 421 Hz), −16.65 (m, 1H, hydride, ²J_{Pt−H} = 23 Hz). ³¹P{¹H} NMR (in CDCl₃): δ = 92.0 (s, 1P, ¹J_{Pt−P} = 2749 Hz).
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