Cluster Compounds

A Highly Unsaturated Platinum–Rhenium Cluster Complex that Adds an Unusually Large Amount of Hydrogen**

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Important results continue to emerge from current research on polynuclear metal cluster complexes.[1] In recent studies we have shown that platinum and palladium groups containing the bulky tri-*tert*-butylphosphine ligand readily add to polynuclear metal cluster complexes to form adducts that are inherently electron deficient around the metal atoms.[2] Herein we present a new example of these complexes that exhibits an unusually high degree of electronic unsaturation that predisposes it to an addition reaction with an unusually large amount of hydrogen.

The new complex $[Pt_3Re_2(CO)_6(PtBu_3)_3]$ (**1**) was obtained in 18 % yield from the reaction of $Pt(PtBu_3)_2$ with $[Re_2(CO)_{10}]$ in refluxing octane (125 °C). The compound was characterized by single-crystal X-ray diffraction methods (Figure 1). The

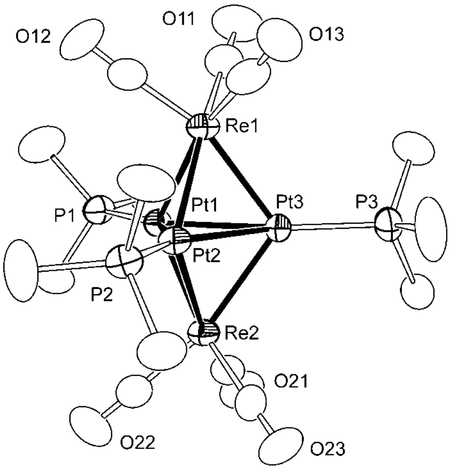

Figure 1. An ORTEP diagram of the molecular structure of **1**, thermal ellipsoids set at 30 % probability. The methyl groups on the $PtBu_3$ ligands have been omitted for clarity. Selected bond lengths [Å]: Pt1-Re1 2.6275(7), Pt2-Re1 2.6728(7), Pt3-Re1 2.6431(7), Pt1-Re2 2.6690(7), Pt2-Re2 2.6158(7), Pt3-Re2 2.6617(7), Pt1-Pt2 2.7202(7), Pt1-Pt3 2.7104(7), Pt2-Pt3 2.7369(7).

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complex contains a trigonal bipyramidal cluster of five metal atoms. The equatorial plane of the cluster is defined by three $\mathrm{Pt(P}t\mathrm{Bu_3)}$ groupings. The two $\{\mathrm{Re(CO)_3}\}$ units occupy the two apical positions. Compound **1** is electronically unsaturated by the amount of 10 valence electrons[3,4] Accordingly, the six Re–Pt bonds are unusually short, they range from 2.6158(7)–2.6728(7) Å. However, the Pt–Pt bonds are about normal, 2.7104(7)–2.7369(7) Å.

To understand the nature of the electronic unsaturation in **1** we have performed Fenske–Hall molecular orbital (MO) calculations.[5] The calculation was setup by using crystal coordinates for all non-hydrogen atoms, and assembling three $\{\mathrm{Pt(PH_3)}\}$ fragments in a trigonal planar arrangement and two $\{\mathrm{Re(CO)_3}\}$ fragments oriented perpendicular to that plane having overall an approximate D_{3h} symmetry. The calculations reveal the existence of five low-lying unoccupied molecular orbitals in the form of a degenerate pair at −3.28 eV having E″ symmetry (the lowest unoccupied molecular orbital; LUMO), a second degenerate pair (LUMO+1) at −1.46 eV having E′ symmetry, and one nondegenerate orbital at −0.79 eV which has A_2'' symmetry. These five orbitals could accommodate the anticipated 10 "missing" valence bonding electrons. The highest occupied molecular orbital (HOMO) of A_1' symmetry lies at −4.65 eV. This orbital is dominated by Pt–Pt bonding in the $\mathrm{Pt_3}$ plane, see Supporting Information for a diagram. The form of one of the degenerate E″ LUMOs is shown in Figure 2. The diagram shows that the contours of the orbital are oriented predominantly along the Re–Pt bonds.

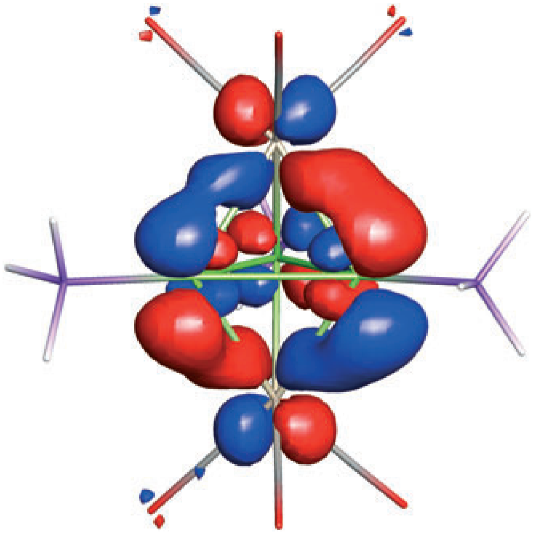

Figure 2. One of the two components of the E″ LUMO of **1**. Cluster shown as stick model; green Pt, brown Re, purple phosphine, red carbonyl.

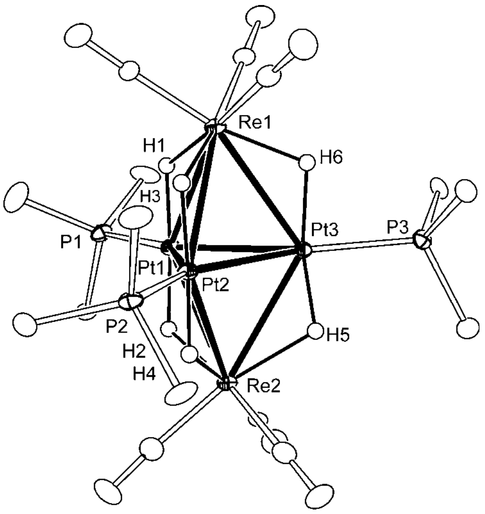

Figure 3. An ORTEP diagram of the molecular structure of **2**, thermal ellipsoids set at 50% probability. Selected bond lengths [Å]: Pt1-Re1 2.9202(3), Pt2-Re1 2.8989(3), Pt3-Re1 2.9004(3), Pt1-Re2 2.9170(3), Pt2-Re2 2.9134(3), Pt3-Re2 2.9050(3), Pt1-Pt2 2.7026(3), Pt1-Pt3 2.7095(3), Pt2-Pt3 2.7259(3), Pt1-H1 1.59(6), Pt1-H2 1.66(6), Pt2-H3 1.62(6), Pt2-H4 1.51(6), Pt3-H5 1.55(6), Pt3-H6 1.66(6), Re1-H1 1.91(6), Re1-H3 1.72(6), Re1-H6 1.89(6), Re2-H2 1.91(6), Re2-H4 1.97(6), Re2-H5 1.94(6).

We have found that **1** reacts with hydrogen, a convenient source of electrons, at room temperature to yield the hexahydrido complex $[\mathrm{Pt_3Re_2(CO)_6(P}t\mathrm{Bu_3)_3(\mu\text{-}H)_6}]$ (**2**) in 90% yield. Compound **2** was also characterized by single-crystal X-ray diffraction (Figure 3). The metal cluster in **2** has a trigonal bipyramidal structure of five metal atoms similar to that of **1**, but it also contains six hydrido ligands arranged in a form having one bridging H ligand on each of the six Re–Pt bonds in the complex. Each of the six hydrido ligands was located and refined in the structural analysis by performing the intensity data collection at 100 K. As expected, the Re–Pt bonds have become significantly longer owing to the presence of the bridging hydrido ligands.[6] A Fenske–Hall MO calculation of **2**, analogous to that of **1**, shows an A_1' HOMO at −5.42 eV similar to that in **1**, but only one LUMO, an E′ that lies at −1.73 eV. The E″ and A_2'' orbitals in **1** are now filled bonding orbitals at −12.75 eV and −11.22 eV, respectively, and contain the six additional electrons that were supplied by the three equivalents of hydrogen. A correlation diagram showing the relationship between these orbitals in **1** and **2** is shown in Figure 4. The metal cluster of **2** is also electron deficient, but only by four electrons.

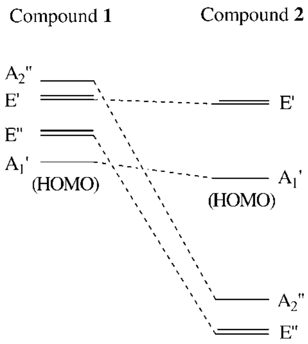

Figure 4. A correlation diagram of the Fenske–Hall MOs of **1** and **2** in D_{3h} symmetry.

There are a few examples where metal complexes condense upon reaction with hydrogen to form polynuclear metal species that contain relatively large amounts of hydrogen,[7] but as far as we know this is the first example of the addition of three equivalents of H_2 by an intact molecular metal-cluster complex.

Platinum-containing bimetallic clusters on supports have recently been shown to exhibit superior properties for hydrogenation catalysis.[8] The addition of hydrogen to **1** under the unusually mild conditions reported herein (25 °C) suggest that it too might have applications as a hydrogenation catalyst. Compound **1** might also serve as a model for hydrogen storage although the addition of hydrogen to **1** is irreversible up to 151 °C.[9]

Experimental Section

1: $Pt(PtBu_3)_2$ (160.0 mg, 0.267 mmol) and $[Re_2(CO)_{10}]$ (29.0 mg, 0.044 mmol) were dissolved in octane (15 mL) and then heated to reflux for 3 h. The brown product was separated by thin layer chromatography (TLC; silica gel) using a 3:1 hexane/methylene chloride solvent mixture to give 13.9 mg (18 % yield). Spectral data for **1**: IR (in hexane): $\tilde{\nu}_{CO} = 1985$ (s), 1892 cm^{-1} (s). ^1H NMR (400 MHz, $[D_8]$toluene, 25 °C, TMS): $\delta = 1.63$ ppm (d, $^3J(P,H) = 13$ Hz, 81 H; CH_3); $^{31}P\{^1H\}$ NMR (162 MHz, $[D_8]$toluene, 25 °C, 85 % *ortho*-H_3PO_4): $\delta = 109.23$ ppm (m, 3 P). Crystal data for **1**: $Re_2Pt_3P_3O_6C_{42}H_{81}\cdot C_6H_{14}$, $M_r = 1818.82$, monoclinic, space group $P2_1/n$, $a = 13.9117(13)$, $b = 24.058(2)$, $c = 18.0919(17)$ Å, $\beta = 92.210(2)°$, $V = 6050.7(10)$ Å^3, $Z = 4$, $T = 296$ K, $Mo_{K\alpha} = 0.71073$ Å. The final $R1(F^2)$ was 0.0501 for 7040 reflections $I > 2\sigma(I)$.

2: Compound **1** (11.6 mg, 0.067 mmol) was dissolved in hexane (25 mL). Hydrogen gas was passed through the stirred solution at 25 °C for 4 h. The product was isolated by TLC (silica gel) using a 3:1 hexane/methylene chloride solvent to yield 10.5 mg (90 %) of orange **2**. Spectral data for **2**: IR (in hexane): $\tilde{\nu}_{CO} = 2009$ (s), 1914 cm^{-1} (vs). ^1H NMR (400 MHz, $[D_8]$toluene, 25 °C, TMS): $\delta = 1.50$ (d, $^3J(P,H) = 13$ Hz, 81 H; CH_3), -4.34 ppm (quartet, $^1J(Pt,H) = 723$ Hz, $^2J(P,H) = 4$ Hz, 6 H; hydrido); $^{31}P\{^1H\}$ NMR (162 MHz, $[D_8]$toluene, 25 °C, 85 % *ortho*-H_3PO_4): $\delta = 111.42$ ppm (m, 3 P). MS. ES$^+$/MS calcd for $M+H$, $[Re_2Pt_3P_3O_6C_{42}H_{87}+H]^+$, 1739, found 1739. Crystal data for **2**: $Re_2Pt_3P_3O_6C_{42}H_{81}\cdot C_6H_6\cdot {}^1/_2C_8H_{18}$, $M_r = 1873.92$, monoclinic, space group $P2_1/n$, $a = 14.7099(6)$, $b = 23.4704(9)$, $c = 17.7176(7)$ Å, $\beta = 91.0310(10)°$, $V = 6116.0(4)$ Å^3, $Z = 4$, $T = 100$ K, $Mo_{K\alpha} = 0.71073$ Å. The final $R1(F^2)$ was 0.0342 for 13055 reflections $I > 2\sigma(I)$. CCDC-260166 (**1**) and CCDC-260167 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Solutions of **2** in nonane were heated to reflux (151 °C) for 1 h. There was no spectroscopic evidence (infrared) for the formation of **1**.

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