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A Highly Unsaturated Platinum–Rhenium Cluster Complex Activates Hydrogen Reversibly**

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We have recently shown that electron-deficient bimetallic carbonyl cluster complexes containing palladium and platinum can be readily obtained from the reactions of metal carbonyl complexes with $[Pd(PtBu_3)_2]$ and $[Pt(PtBu_3)_2]$.[1] The success of this reaction is, undoubtedly, due in part to ligand deficiencies caused by steric effects of the very bulky tri-*tert*-butylphosphine ligand. Metal complexes of the noble metals are also of interest for their ability to activate and store large quantities of hydrogen.[2] Hydrogen-storage applications require the hydrogen additions to be reversible. We have recently shown that the highly electron-deficient platinum–rhenium complex $[Pt_3Re_2(CO)_6(PtBu_3)_3]$ (**1**) is capable of adding three equivalents of hydrogen at room temperature to form the hexahydrido complex $[Pt_3Re_2(CO)_6(PtBu_3)_3(\mu\text{-}H)_6]$ (**2**) which contains a bridging hydrido ligand on each of its six Pt−Re bonds [Eq. (1)].[3] This addition reaction is thermally

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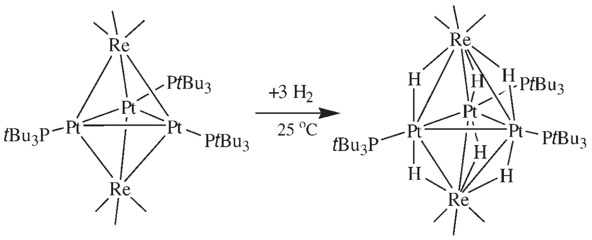


(1)

1 **2**

irreversible. Herein we report a new member of this family of unsaturated platinum–rhenium cluster complexes that not only exhibits an unusual ability to activate hydrogen under mild conditions, but also does it reversibly.

Two new compounds: $[PtRe_2(CO)_9(PtBu_3)(\mu\text{-}H)_2]$ (**3**; 35% yield) and $[Pt_2Re_2(CO)_7(PtBu_3)_2(\mu\text{-}H)_2]$ (**4**; 24% yield), were obtained from the reaction of $[Pt(PtBu_3)_2]$ with $[Re_3(CO)_{12}(\mu\text{-}H)_3]$ in hexane heated to reflux for 2 h. Compound **3** contains a simple $PtRe_2$ triangular cluster with two bridging hydrido ligands (see Supporting Information for ORTEP diagram). It is related to a number of similar compounds that have been reported.[4]

Compound **4** contains four metal atoms: two of platinum and two of rhenium. The molecular structure of **4** was established crystallographically. The compound crystallizes with three independent molecules in the crystallographic asymmetric unit. Due to molecular disorder (see Supporting Information), the quality of this structural analysis is not high. All three molecules are structurally similar and an ORTEP diagram of the molecular structure of one of them is shown in Figure 1. The four metal atoms are arranged in the shape of a tetrahedron. There are seven carbonyl ligands: each rhenium atom is bound to three of them and one is bonded to one of the two platinum atoms. Each platinum atom has one $PtBu_3$ ligand. The compound contains two hydrido ligands as confirmed by its mass and variable temperature (VT) ^1H NMR spectra. The hydrido ligands were not located in the structural analysis, but the ^1H NMR spectrum recorded at −40 °C exhibits two highly shielded resonances at $\delta = -0.87$ (s, 1 H, hydride), −2.05 (dd, $^2J(P,H) = 6$ Hz, $^2J(P,H) = 11$ Hz, $^1J(Pt,H) = 621$ Hz, 1 H, hydride) that can be attributed to them. The first resonance exhibits no couplings to ^{195}Pt or ^{31}P of the phosphine ligands. This ligand probably bridges the Re−Re bond. The second resonance is coupled to both phosphine ligands and ^{195}Pt. This hydrido ligand may bridge the Pt−Pt bond; however, we can not rule out that it could be a terminal ligand as found in compound **5**, see below. The hydrido ligands in **4** are dynamically active as shown by the VT ^1H NMR spectra shown in Figure 2. The $^{31}P\{^1H\}$ NMR spectrum of **4** at −25 °C shows two resonances of equal intensity with mutual couplings and couplings to ^{195}Pt, $\delta = 85.5$ (d, $^3J(P,P) = 82$ Hz, $^1J(Pt,P) = 3880$ Hz, 1 P), 112.7 ppm (d, $^3J(P\text{-}P) = 82$ Hz, $^1J(Pt,P) = 2435$ Hz, 1 P) consistent with the structure as found in the solid state. The ^{31}P resonances are broad at room temperature and the ^{31}P couplings between the two resonances are not observed. This situation is suggestive of yet another dynamic exchange process, and these resonances do broaden still further at higher temperatures, but the averaged spectrum was not attained at 108 °C and the compound decomposed significantly at higher

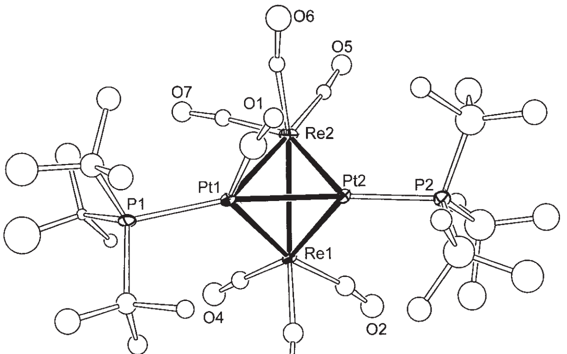


Figure 1. An ORTEP diagram of the molecular structure of one of the three independent molecules in the unit cell of the crystal of **4**, thermal ellipsoids set at 40% probability. Hydrogen atoms are not shown. The hydrido ligands were not located in the structural analysis. Selected interatomic distances [Å]: Molecule 1: Pt1-Pt2 2.6665(16), Pt1-Re1 2.9100(15), Pt1-Re2 2.8648(16), Pt2-Re1 2.7259(15), Pt2-Re2 2.6119(15), Re1-Re2 2.9419(13), Molecule 2: Pt3-Pt4 2.6738(16), Pt3-Re3 2.8662(15), Pt3-Re4 2.9152(16), Pt4-Re3 2.6144(15), Pt4-Re4 2.7019(16), Re3-Re4 2.9388(14), Molecule 3: Pt5-Pt6 2.6646(17), Pt5-Re5 2.8972(18), Pt5-Re6 2.8674(18), Pt6-Re5 2.7116(18), Pt6-Re6 2.6139(18), Re5-Re6 2.921(2).

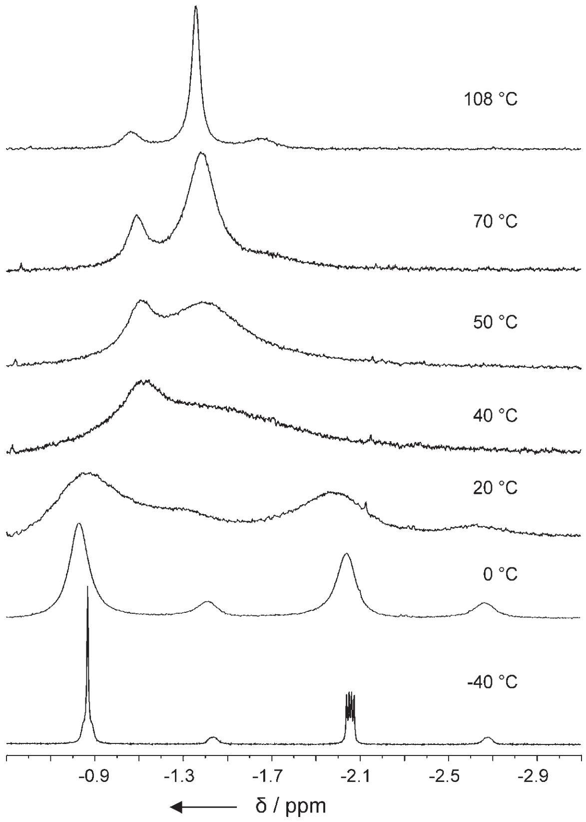
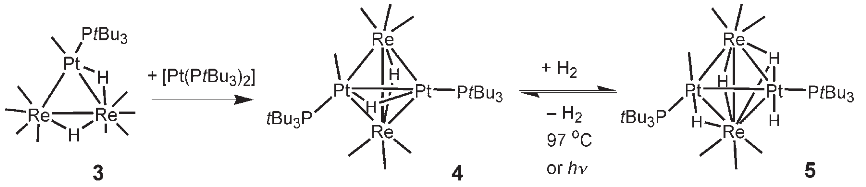


Figure 2. ^1H NMR spectra at 500 MHz of compound **4** in the hydride region at various temperatures in [D$_8$]toluene solvent.

temperatures. A simple exchange of the terminal carbonyl ligand on atom Pt1 between the two platinum atoms could account for the broadening effects observed in these ^{31}P resonances. Significantly, the cluster of **4** contains only 54 valence electrons. This number is six less than the 60 required for a tetrahedral cluster in which all the metal atoms obey the 18 electron rule. Although there are other {Pt$_2$M$_2$} compounds with less than 60 electrons,[5] having as few as 54 electrons is very unusual. Compound **4** can also be obtained from **3** by further treatment with [Pt(P*t*Bu$_3$)$_2$], see Scheme 1.



Scheme 1.

It was found that **4** adds one equivalent of H$_2$ (1 atm/ 25 °C) to yield the new tetrahydrido compound [Pt$_2$Re$_2$(CO)$_7$-(P*t*Bu$_3$)$_2$(μ-H)$_4$] (**5**) in 71 % yield. Compound **5** was also characterized crystallographically. This compound has only one formula equivalent in the asymmetric crystal unit and a very high quality structural analysis was obtained which included the location and refinement of all four of the hydrido ligands (Figure 3). The structure of **5** is very similar to that of **4** except that it has four hydrido ligands. One of the hydrido ligands H1 bridges the Re−Re bond (as similarly proposed for **4**). H2 is a triple bridge on the Pt2-Re1-Re2 triangle. H3 bridges the Pt1−Re1 bond and H4 is a terminal ligand on Pt2. As expected, the addition of hydrido ligands to the bonds Pt1−Re1 and Pt2−Re2 leads to an increase in the metal–metal bond distances compared to those in **4**.[6]

The ^{1}H NMR spectrum of **5** exhibits only three resonances for the four hydrido ligands, $\delta = -2.13$ (s, ^2J(Pt,H) = 37 Hz, 1 H), −2.34 (d, ^1J(Pt,H) = 588 Hz, ^2J(P,H) = 12 Hz, 1 H), −6.10 (dd, ^1J(Pt,H) = 801 Hz, ^2J(Pt,H) = 43 Hz, ^2J(P,H) = 10 Hz, ^3J(P,H) = 3 Hz, 2 H). The resonance at $\delta = -6.10$ (2 H) indicates that two of the hydrido ligands are selectively averaged. These remain averaged throughout the temperature range −90 °C to 110 °C.

When solutions of **5** in heptane were heated to reflux for 3 h in the presence of a slow purge of nitrogen, compound **4** was regenerated in high yield (90 % isolated) by loss of H$_2$ (confirmed by ^{1}H NMR spectroscopy). Most interestingly, however when solutions of **5** were irradiated (UV/Vis) at room temperature in the presence of a slow purge of nitrogen for 4 h, compound **4** was also formed in high yield (83 % isolated) by loss of H$_2$ (also confirmed by ^{1}H NMR spectroscopy).

The photochemical elimination of hydrogen from mononuclear metal complexes is well known,[7] but we are unaware of any reports of the photoelimination of hydrogen from polynuclear metal cluster complexes. Goodfellow et al. have described the addition of hydrogen to some highly unsaturated tetraplatinum compounds containing P*t*Bu$_3$ ligands under mild conditions; the hydrogen could be removed from them by treatment with ethylene.[8]

Bimetallic materials have attracted attention for hydrogen-storage applications.[9] Bimetallic nanoclusters have attracted considerable attention because of their ability to function as highly active hydrogenation catalysts when placed on supports.[10] Platinum–rhenium bimetallic catalysts are widely used by the petroleum industry because of their superior properties for the important process known as reforming.[11] Unusual electronic and reactivity properties of these new electron-deficient platinum–rhenium cluster complexes[3] suggest that this combination of metals has special features that could be important for future applications to the hydrogen industry and hydrogenation catalysis. Further studies of the mechanism of this unusual reversible reaction with hydrogen are in progress.

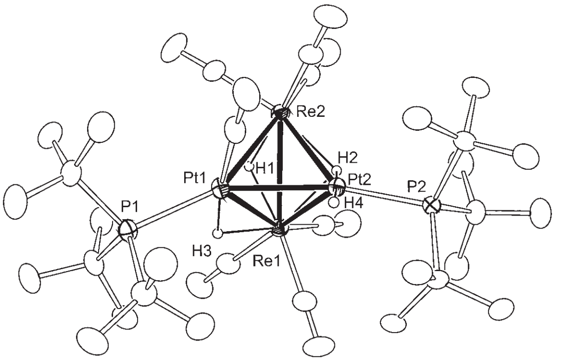


Figure 3. An ORTEP diagram of the molecular structure of **5**, thermal ellipsoids set at 40 % probability. Selected interatomic distances [Å]: Pt1-Pt2 2.7025(2), Pt1-Re1 2.9732(2), Pt1-Re2 2.8805(2), Pt2-Re1 2.9182(2), Pt2-Re2 2.7866(2), Re1-Re2 2.8303(3), Pt1-H3 1.50(7), Pt2-H2 1.78(6), Pt2-H4 1.51(5), Re1-H1 1.74(4), Re1-H2 2.03(6), Re1-H3 2.02(7), Re2-H1 1.89(4), Re2-H2 1.95(6), Pt1-P1 2.3909(10), Pt2-P2 2.2729(9).

Experimental Section

Reaction of [Re$_3$(CO)$_{12}$(μ-H)$_3$] with [Pt(P*t*Bu$_3$)$_2$]: [Pt(P*t*Bu$_3$)$_2$] (30.0 mg, 0.050 mmol) and [Re$_3$(CO)$_{12}$(μ-H)$_3$] (23.0 mg, 0.026 mmol) were dissolved in hexane (40 mL) and then heated to reflux for 2 h. After cooling, the solvent was removed in vacuo, and the products were separated by thin-layer chromatography (TLC; on silica gel) using a 3:1 hexane/CH$_2$Cl$_2$ solvent mixture to yield, in order of elution: 9.2 mg (35 % yield) of yellow [PtRe$_2$(CO)$_9$(P*t*Bu$_3$)(μ-H)$_2$] (**3**), 1.8 mg of an uncharacterized purple band, and 8.4 mg (24 % yield) of red [Pt$_2$Re$_2$(CO)$_7$(P*t*Bu$_3$)$_2$(μ-H)$_2$] (**4**). Spectral data for **3**: IR ν_{CO} (in hexane): $\tilde{\nu} = 2101$ (m), 2070 (s), 2008 (vs), 1991 (m), 1982 (m), 1972 (m), 1958 (s), 1950 cm^{-1} (m). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, TMS): $\delta = 1.53$ (d, ^3J(P, H) = 13 Hz, 27 H, CH$_3$), −7.19 (d, ^2J(P,H) = 14 Hz, ^1J(Pt, H) = 538 Hz, 1 H, hydride), −15.41 ppm (s, ^2J(Pt, H) = 31 Hz, 1 H, hydride); ^{31}P{^{1}H} NMR (400 MHz, CDCl$_3$, 25 °C, 85 % *ortho*-H$_3$PO$_4$): $\delta = 110.6$ ppm (s, ^1J(Pt,P) = 2936 Hz, 1 P). Elemental analysis (%) calcd: C 24.63, H 2.76; found: C 25.31, H 2.72. Crystal data for **3**: PtRe$_2$PO$_9$C$_{21}$H$_{29}$, M_r = 1023.90, monoclinic, space group *C*2/*c*, $a = 27.395(3)$, $b = 14.3333(16)$, $c = 19.087(2)$ Å, $\beta = 130.348(2)°$, $V =$

5711.9(11) Å^3, $Z=8$, $T=294$ K, $\mathrm{Mo_{K\alpha}}=0.71073$ Å. The final $R1(F^2)$ was 0.0385 for 6066 reflections $I>2\sigma(I)$. Spectral data for **4**: IR ν_{CO} (in CH_2Cl_2): $\tilde{\nu}=2035$ (w), 2015 (m), 1994 (vs), 1916 (m, sh), 1900 cm^{-1} (s, br). ^{1}H NMR (500 MHz, [D$_8$]toluene, −40 °C, TMS): $\delta=1.20$ (broad, 27 H, CH$_3$), −0.87 (s, 1 H, hydride), −2.05 ppm (dd, ^2J(P,H) = 6 Hz, ^2J(P,H) = 11 Hz, ^1J(Pt,H) = 621 Hz, 1 H, hydride). ^{31}P{^{1}H} NMR (202.5 MHz, [D$_8$]toluene, −25 °C, 85 % *ortho*-H$_3$PO$_4$): $\delta=85.5$ (d, ^3J(P,P) = 82 Hz, ^1J(Pt,P) = 3880 Hz, 1 P), 112.7 ppm (d, ^3J(P-P) = 82 Hz, ^1J(Pt,P) = 2435 Hz, 1 P). Mass Spectrometry: ES$^+$/MS calcd for M^+, $[Pt_2Re_2(CO)_7(PtBu_3)_2(\mu\text{-}H)_2]^+$, 1365, found 1365. Elemental analysis (%) calcd: C 27.27, H 4.14; found: C 27.27, H 3.90. Crystal data for **4**: $Pt_2Re_2P_2O_7C_{31}H_{54}$, $M_r=1363.26$, orthorhombic, space group $P2_12_12_1$, $a=15.2359(14)$, $b=15.2464(14)$, $c=50.847(5)$ Å, $V=11811.3$ (19) Å^3, $Z=12$, $T=100$ K, $\mathrm{Mo_{K\alpha}}=0.71073$ Å. The final $R_1(F^2)$ was 0.0734 for 17760 reflections $I>2\sigma(I)$.

Reaction of **3** with Pt(P*t*Bu$_3$)$_2$: [Pt(P*t*Bu$_3$)$_2$] (30.0 mg, 0.050 mmol) was added to a solution of **3** (10.4 mg, 0.010 mmol) in hexane (25 mL). The reaction mixture was heated to reflux for 8 h, after which the solvent was removed in vacuo. The products were separated by TLC (silica gel) using a 3:1 hexane/CH$_2$Cl$_2$ solvent mixture to yield, in order of elution: 6.0 mg (58 % yield) of starting yellow **3**, and 3.0 mg (22 % yield) of red $[Pt_2Re_2(CO)_7(PtBu_3)_2(\mu\text{-}H)_2]$ (**4**).

Addition of H$_2$ to **4**: Compound **4** (16.1 mg, 0.012 mmol) was dissolved in heptane (30 mL). With stirring, hydrogen gas was passed through the solution at room temperature for 12 h. The heptane solvent was then removed in vacuo and the product was isolated by TLC (silica gel) using a 3:1 hexane/ CH$_2$Cl$_2$ solvent mixture to yield 11.5 mg (71 %) of bright-orange $[Pt_2Re_2(CO)_7(PtBu_3)_2(\mu\text{-}H)_4]$ (**5**) as the major product. Spectral data for **5**: IR ν_{CO} (in Hexane): $\tilde{\nu}=2041$ (m), 2028 (s), 2006 (vs), 1936 (s), 1927 (vs), 1918 cm^{-1} (m, sh). ^{1}H NMR (400 MHz, [D$_8$]toluene, 25 °C, TMS): $\delta=1.29$ ppm (d, ^3J(P,H) = 13 Hz, 27 H, CH$_3$), 1.27 ppm (d, ^3J(P,H) = 13 Hz, 27 H, CH$_3$), −2.13 (s, ^2J(Pt,H) = 37 Hz, 1 H, hydride), −2.34 (d, ^1J(Pt,H) = 588 Hz, ^2J(P,H) = 12 Hz, 1 H, hydride), −6.10 ppm (dd, ^1J(Pt,H) = 801 Hz, ^2J(Pt,H) = 43 Hz, ^2J(P,H) = 10 Hz, ^3J(P,H) = 3 Hz, 2 H, hydride). ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]toluene, 25 °C, 85 % *ortho*-H$_3$PO$_4$): 95.75 ppm (d, ^3J(P,P) = 62 Hz, ^1J(Pt,P) = 3388 Hz, ^2J(Pt,P) = 197 Hz, 1 P), 108.14 ppm (d, ^3J(P,P) = 62 Hz, ^1J(Pt,P) = 2720 Hz, ^2J(Pt,P) = 296 Hz, 1 P). Mass Spectrometry ES$^+$/MS calcd for M^+, $[Pt_2Re_2(CO)_7(PtBu_3)_2(\mu\text{-}H)_4]^+$, 1367, found 1367. Elemental analysis (%) calcd: C 27.23, H 4.28; found: C 27.64, H 3.99. Crystal data for **5**: $Pt_2Re_2P_2O_7C_{31}H_{58}\cdot 1/2\,CH_2Cl_2$, $M_r=1409.76$, monoclinic, space group $P2_1/c$, $a=14.7121(9)$, $b=17.2332(11)$, $c=17.1146(11)$ Å, $\beta=105.0020(10)°$, $V=4191.3(5)$ Å^3, $Z=4$, $T=294$ K, $\mathrm{Mo_{K\alpha}}=0.71073$ Å. The final $R_1(F^2)$ was 0.0198 for 9236 reflections $I>2\sigma(I)$. CCDC 286932–286934 (**3**–**5**) 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.

Thermal elimination of hydrogen from **5**: Compound **5** (12.8 mg, 0.009 mmol) was dissolved in heptane (60 mL) in a 100 mL three-neck flask equipped with a reflux condenser and a gas inlet. A slow stream of nitrogen (flow rate ≈27 mL min^{-1}) was allowed to flow through the flask while refluxing this solution for 3 h. The heptane solvent was then removed in vacuo and the products were separated by TLC (silica gel) using a 3:1 hexane/CH$_2$Cl$_2$ solvent mixture to yield, in order of elution: 0.7 mg (5 % yield) of unchanged **5**, and 11.5 mg (90 % yield) of **4**.

Photoelimination of hydrogen from **5**: Compound **5** (12.8 mg, 0.009 mmol) was dissolved in hexane (60 mL) in a 100 mL three-neck flask equipped with a reflux condenser and a gas inlet. A slow stream of nitrogen (flow rate ≈27 mL min^{-1}) was allowed to flow through the flask while irradiating this solution for 4 h. The progress of this reaction can be monitored by IR. The hexane solvent was then removed in vacuo and the products were separated by TLC (silica gel) using a 3:1 hexane/CH$_2$Cl$_2$ solvent mixture to yield, in order of elution: 1.0 mg (8 % yield) of unchanged **5**, and 10.6 mg (83 % yield) of **4**. There were a few uncharacterized bands present on the TLC plate in trace amounts (< 1 mg).

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