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Reaction of Platinum–Gold Cluster Compounds with Dihydrogen

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The reactivity of metal cluster compounds toward H_2 and the structures and properties of hydride-containing cluster compounds are important because they should provide a better understanding of homogeneous and heterogeneous catalytic processes.[1] Hydrido compounds of heterometallic clusters that contain gold have been described, and the presence of hydride bridges between gold and the hetero metal is well documented.[2–6] In $[Ru(dppm)_2(\mu\text{-}H)_2(AuPPh_3)_2]^+$ [2] and $[Ir(triphos)(Cl)(\mu\text{-}H)(AuPPh_3)_2]^+$ [3] the bridging hydrides have been directly observed by X-ray diffraction, while in $[Ir(PPh_3)_2(H)_2(AuPPh_3)_4]^+$,[4] $[Pt(PPh_3)(H)(AuPPh_3)_7]^{2+}$,[5] and others the bonding positions of the hydrides have been proposed to be bridging from spectroscopic data, the solid-state molecular geometry of the non-hydrogen atoms, and potential energy calculations.[6]

Platinum–gold cluster compounds have recently been reported to be very active catalysts for the H_2–D_2 equilibration reaction.[7] These clusters therefore have great potential to serve as models for the activation of H_2 by supported Pt–Au catalysts. This observation has prompted us to investigate the reactivity of some Pt–Au clusters toward H_2 in more detail. We report here the results for the cluster $[Pt(AuPPh_3)_8](NO_3)_2$ (**1**). This is a well-studied cluster which has a Pt-centered, crown-shaped geometry in the solid state.[8] Its solution chemistry is characterized by reversible electrochemical processes and by nucleophilic, electrophilic, and oxidative addition reactions.[9] This cluster is also an excellent H_2–D_2 equilibration catalyst with a turnover frequency for HD formation of 1 s^{-1} at 30 °C and 1 atm pressure in the solid state.[7] The 16/18-electron counting rule has proved to be a reliable guide for understanding structures and reactivities of M–Au and Au cluster compounds.[6,8–10] We will show here that the 16-electron cluster **1** reacts rapidly and fully reversibly at ambient temperature and pressure with H_2 in solution and in the solid state. This is an unusual and important observation in cluster chemistry as there are very few examples of facile H_2 activation by transition metal clusters.[1c]

The reaction can be followed at room temperature and ca. 1 atm of H_2 pressure in dichloromethane solution and in the solid state. Solutions of **1** turn from dark brown to orange-red almost immediately when a N_2 atmosphere is replaced with H_2. After substitution of the H_2 by N_2 or Ar the original color reappears in a few minutes. A similar reversible color change was observed with solid samples of **1** and corresponded to reversible H_2 uptake (vide infra).

These changes were followed in CH_2Cl_2 solution by UV–vis and NMR spectroscopy and by electrochemistry.[11] All observations and data in the solution phase can be interpreted with the following reaction scheme:

$$[Pt(AuPPh_3)_8]^{2+}\ (\mathbf{1}) + H_2 \rightleftarrows [Pt(H)_2(AuPPh_3)_8]^{2+}\ (\mathbf{2}) \qquad (1)$$

The NMR spectra for a CD_2Cl_2 solution of **1** in the presence of H_2 show a significant dependence on temperature and H_2 pressure, and the changes are completely reversible upon removal of H_2. Some typical spectra are illustrated in Figure 1. At about 1 atm of H_2 pressure signals due to **1** and **2** are clearly evident. The NMR data for **2** [^{195}Pt, δ = -5994 ppm, $^2J_{Pt-P}$ = 380 Hz (nonet), $^1J_{Pt-H}$ = 645 Hz (triplet); ^{31}P, δ = 51.5 ppm, $^2J_{Pt-P}$ = 380 Hz; ^1H (–30 °C, hydride), δ = 3.9 ppm, $^1J_{Pt-H}$ = 645 Hz, $^3J_{P-H}$ = 13.7 Hz (nonet)] are distinctly different from that of **1** [^{195}Pt, δ = -4528 ppm, $^2J_{Pt-P}$ = 497 Hz (nonet); ^{31}P, δ = 55.4 ppm, $^2J_{Pt-P}$ = 497 Hz]. The ^{195}Pt chemical shift for **2** is characteristic of an 18-electron cluster.[12] The presence of hydride ligands is clearly indicated in the ^1H and ^{195}Pt spectra with the H chemical shift and J_{Pt-H} in the region for well-known Pt–Au hydrides like $[Pt(PPh_3)(H)(AuPPh_3)_7]^{2+}$ (δ = 2.26 ppm, $^1J_{Pt-H}$ = 537 Hz),[5a] $[Pt(PPh_3)(H)(AuPPh_3)_6]^+$ (δ = 0.34 ppm, $^1J_{Pt-H}$ = 687 Hz),[5b] and $[Pt(H)(AuPPh_3)_8]^+$ (δ = 5.4 ppm, $^1J_{Pt-H}$ = 705 Hz).[5b] The nonet Pt–P and H–P coupling patterns indicate the presence of eight AuP units, like in the parent compound **1**. The triplet Pt–H coupling pattern observed in the phosphorus decoupled ^{195}Pt NMR

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(11) UV–vis spectra were recorded at room temperature with CH_2Cl_2 as solvent on 10^{-4} M solutions of **1** under an atmosphere of N_2 or H_2. The spectral changes are reversible between the two gas atmospheres [λ_{max}, nm (log ϵ_{max}) under N_2 in 350–600-nm range: 354 (4.71), 400 (4.25), 431 (4.35), 482 (3.93), 515 (br sh, 3.57); under H_2, 356 (4.57), 399 (4.27), 428 (4.24), 480 (3.80)]. ^1H NMR data were recorded at 300 MHz (TMS internal standard) with use of a Varian VXR-300 MHz spectrometer. $^{31}P\{^1H\}$ NMR data were recorded at 121.5 MHz or at 81.02 MHz (TMP internal standard with positive shifts in ppm downfield) with use of the above Varian instrument or a Bruker WM-200 spectrometer. $^{195}Pt\{^1H, ^{31}P\}$ NMR data were recorded at 43.02 MHz ($PtCl_6^{2-}$ in D_2O as external standard) with use of the above Bruker instrument. All NMR data were obtained at ambient temperature unless stated otherwise. Cyclic voltammograms and pulse and differential pulse voltammograms were recorded with use of CH_2Cl_2 solutions 10^{-4} M in **1** and 10^{-2} M in Bu_4NPF_6 as supporting electrolyte. A standard three-electrode cell with a Pt working electrode was used. The same results were obtained with a Au working electrode. The cell was purged with either N_2, Ar, H_2, or D_2.

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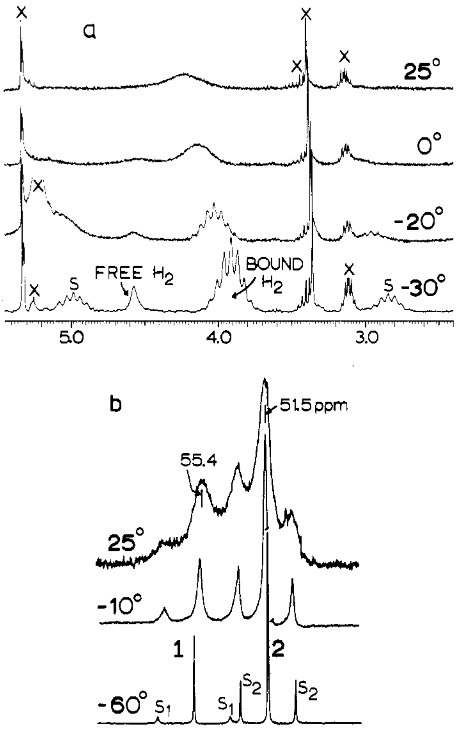

Figure 1. ^1H (a) and ^{31}P (b) NMR spectra at different temperatures for a CD_2Cl_2 solution of 1 saturated with H_2 in a sealed NMR tube. Peaks labeled with X are due to solvent impurities. Peaks labeled with S are ^{195}Pt satellites of the bound H_2.

spectrum clearly indicates the presence of two hydride ligands in **2**. The hydride signal in the ^1H NMR is broad at room temperature due to exchange with free H_2. At lower temperatures the free H_2 and the bound hydride resonances are resolved and sharpen as shown in Figure 1a. A T_1 measurement of the −30 °C spectrum in Figure 1a gives a value of 700 ms for the bound hydride peak. This is similar to the value of 600 ms measured for $[Pt(PPh_3)(H)(AuPPh_3)_7]^{2+}$ at 25 °C and confirms the classical nature of the hydride bonding in **2**.[13] The CH_2Cl_2 solution IR spectrum of **1** under ca. 1 atm of H_2 shows no evidence of terminal M–H stretching vibrations. We therefore tentatively assign a bridging bonding mode to the hydride ligands in accord with observations made on other M–Au hydrido clusters.[2–6] A more thorough IR analysis of solid samples of **1** under atmospheres of N_2, H_2, and D_2 is in progress.

At room temperature and a partial pressure of H_2 of about 0.1 atm over a CH_2Cl_2 solution of **1**, the ^{31}P NMR signals of **1** broaden significantly. The width of these signals increases further with increasing pressures up to about 1 atm, and broad signals due to **2** grow in (Figure 1b). We conclude that this broadening is due to the interconversion of **1** and **2**, which is of intermediate rate at room temperature on the NMR time scale. These signals sharpen as the temperature is decreased to about −60 °C (Figure 1b), indicating that the interconversion of **1** and **2** is slow at this temperature. At room temperature and H_2 pressures between 5 and 30 atm, only sharp signals of **2** are present in the ^{31}P NMR spectrum indicating that **1** is completely converted into **2**.

Voltammetric studies[11] confirm the picture outlined above in showing a CE mechanism for the reduction of **1** in CH_2Cl_2 solution under an atmosphere of H_2. The chemical (C) step is assigned as reaction 1 and the electrochemical reaction (E) is the two-step reversible reduction of **1** to $[Pt(AuPPh_3)_8]^+$ and $[Pt(AuPPh_3)_8]^0$.[14] Identical results are obtained when D_2 is used in place of H_2. The electrochemical analysis is complicated and will be reported in detail elsewhere. Hydrogen uptake measurements on powdered, solid samples of **1** show that 0.7 ± 0.1 mol of H_2 is chemically adsorbed per mole of cluster at 25 °C and 1 atm total pressure.[15] This reaction is reversible. This result suggests that a similar reaction to that shown in (1) occurs in the solid state.

The fast H_2–D_2 equilibration catalysis observed for **1**[7] in nitrobenzene solution (turnover frequency = 0.065 s^{-1} at 30 °C and ca. 1 atm total pressure) and as a molecular solid can be explained by the reversible interaction of a second H_2 or D_2 molecule with the 18-electron compound **2** with fast H–D exchange. This general hypothesis is supported by the observation that the 18-electron, hydride cluster $[Pt(PPh_3)(H)(AuPPh_3)_7](NO_3)_2$ is a better H_2–D_2 equilibration catalyst than **1** in NO_2Ph solution (turnover frequency = 0.12 s^{-1} at 30 °C and 1 atm total pressure).[16] Compound **1** has also been shown to be a good catalyst in the solid state for the hydrogenation of oxygen. The reaction $2D_2 + O_2 \rightarrow 2D_2O$ was monitored by mass spectroscopy and has a rate which is similar to that observed for H_2–D_2 equilibration.[17] Work in progress is directed to the determination of the mechanisms of these catalytic reactions for a series of Pt–Au cluster compounds. We have also found some catalytic activity for the hydrogenation of ethylene to ethane with **1** in the solid state and in methanol solution, but the rates are extremely slow (turnover frequency = 5×10^{-5} s^{-1}).[18] In a previous paper we reported that solid samples of **1** were inactive for ethylene hydrogenation.[7] This reaction had not been observed because the rate is more than 4 orders of magnitude slower than for H_2–D_2 equilibration, and the amount of ethane produced, under the conditions of the original experiment, was undetectable.

The results presented above raise the expectation that other 16-electron M–Au clusters will show a similar reactivity toward H_2. Preliminary studies indicate that the clusters $[Pt(AuPPh_3)_8(CuCl)]^{2+}$ [12] and $[Pt(AuPPh_3)_8(Ag)]^{3+}$ [10f] rapidly and irreversibly take up H_2 at room temperature and 1 atm pressure to give hydride products. Details of these and similar reactions are under study and will be reported in the near future.

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(15) Gas uptake values for 500-mg powdered, solid samples were calculated from pressures measured in a closed, glass reactor (vol = 80 mL) with use of a capacitance manometer (precision ± 0.2 Torr) for additions of known amounts of H_2 and He (used as a control) to evacuated samples up to a total pressure of about 1 atm. The amount of chemically adsorbed H_2 was calculated as the difference between the moles of H_2 adsorbed for **1** and the isoelectronic, inert cluster $[Au(AuPPh_3)_8](NO_3)_3$. The value reported was determined after ca. 15 min of equilibration, although nearly all of the H_2 was adsorbed within the first 5 min. The same value was determined by taking the difference between the amount of H_2 and He adsorbed for **1**.

(16) The turnover frequency was determined in an identical manner as reported in ref 7.

(17) The $O_2 + D_2$ reaction was carried out at 30 °C in a closed, 36-mL glass reactor charged with 5 mg of powdered **1** and a total gas pressure of about 1 atm. The initial gas ratio was $D_2/O_2 = 0.90$. Analysis of the formation of D_2O was carried out with use of a mass spectrometer connected to the reactor by a 75-μm, fused silica capillary tube. The reaction was followed to about 75% conversion, and the rate was only qualitatively determined. A similar reaction occurs for H_2 but measurement of the quantitative formation of H_2O is difficult due to the large background peak at 18 amu (H_2O) in the mass spectrometer.

(18) The hydrogenation of ethylene was carried out at 20 °C in a closed, 12-mL glass reactor charged with 50 mg of powdered **1** as solid sample or in methanol solution and a total pressure of about 1 atm. The initial gas mixture was 50% H_2 and 50% ethylene. Analysis of ethylene and ethane was carried out by a gas chromatograph. Reactions were followed to about 20% conversion.