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Platinum-Gold Cluster Catalysts for D_2(gas)/H_2O(liquid) Isotope Exchange

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Platinum-gold cluster compounds are excellent catalysts for H_2/D_2 equilibration ($H_2 + D_2 = 2HD$) under homogeneous and heterogeneous (gas-molecular solid) conditions.[1-3] For example, turnover rates for HD production with use of $[Pt(AuPPh_3)_8](NO_3)_2$ as the catalyst are 4.5 and ca. 300 min^{-1} for homogeneous (nitrobenzene solution) and heterogeneous (gas-molecular solid) conditions (1 atm total pressure and 30 °C), respectively. The homogeneous H_2/D_2 equilibration is clean with no exchange of D_2 with the PPh_3 ligands or the solvents acetonitrile, acetone, and nitrobenzene. No H/D exchange was observed with water or ethanol, when added to the above solvents.[1,3] The first step of the mechanism of this catalysis reaction is the reversible addition of H_2 to $[Pt(AuPPh_3)_8]^{2+}$ as shown in eq 1.[2,3] This equilibrium reaction has been directly observed by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy in solution under 1 atm of H_2.[2,3] T_1 measurements

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

for the coordinated hydrido ligands in $[Pt(H)_2(AuPPh_3)_8]^{2+}$ show that they are classically bound and not η^2-H_2. There is also good evidence that the hydride ligands are in bridging positions.[2,3]

We have recently discovered a new and potentially useful, homogeneous, catalytic reaction. In pyridine solution, the cluster $[Pt(AuPPh_3)_8]^{2+}$ showed surprisingly fast exchange between D_2(gas) and H_2O(liquid). Thus, reaction of D_2 with a pyridine solution of the cluster that contained some H_2O[4] gave fast production of H_2 and HD (turnover rate = 1.5 min^{-1} at 1 atm total pressure and 30°C, Table 1). A typical reaction profile is shown in Figure 1.[5] Data for the control reaction carried out with wet nitrobenzene (saturated with H_2O) as solvent, where $(D_2)_g/(H_2O)_l$ exchange did not occur, are included in Figure 1. Exchange was also not observed between $(D_2)_g$ and $(H_2O)_l$ with the (1:4 v/v) solvent mixtures H_2O-acetone or H_2O-methanol, run under the same conditions. Detailed reaction conditions are given in the figure caption. The exchange occurred with water and not with the pyridine solvent. Equilibrium was reached in about 12 h, and the relative amounts of D_2, HD, and H_2 at equilibrium (shown in Figure 1) were in approximate agreement with the initial amounts of D_2 and H_2O in the reactor.[6] The cluster $[Pt(PPh_3)(AuPPh_3)_6]^{2+}$ also catalyzed $(D_2)_g/(H_2O)_l$ exchange but at much slower rates.

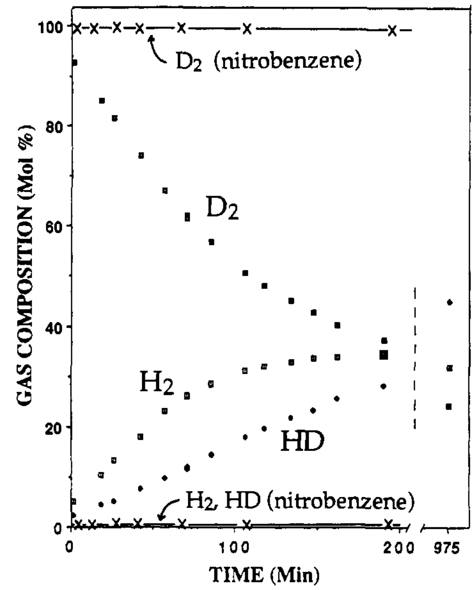

Figure 1. Composition of the head space gas in mole percent D_2, HD, and H_2 as a funtion of time for reaction of D_2 (1.3 mmol) with H_2O (0.6 mmol) in the presence of $[Pt(AuPPh_3)_8](NO_3)_2$ (4.0×10^{-3} mmol) in pyridine and nitrobenzene (---X---) solutions. The reactions were carried out in a closed, 38 mL reactor with 6 mL of rapidly stirred solution maintained at 1 atm total pressure and 30°C. The points at the far right (975 min) are the mole percents for the reaction in pyridine close to equilibrium.

Although $(D_2)_g/(H^+)_l$ exchange is known for a number of organometallic hydrides[7] (notably of the η^2-H_2 variety) and for hydrogenase enzymes,[8] there are several factors which make this cluster-based system unusual. The exchange occurs between D_2 and water whereas with many metal-complex-based systems the exchange has only been reported between D_2 and alcohols (typically *t*-BuOH, EtOH, or MeOH). For exchange with water, the rate is at least 2 orders of magnitude faster with $[Pt(AuPPh_3)_8]^{2+}$ than with monometallic complexes, although some faster rates have been observed with alcohols (see Table 1). $[Pt(AuPPh_3)_8]^{2+}$ is stable under the catalytic conditions and can carry out thousands of turnovers, while many organometallic hydrides are not stable in the presence of water. The phosphine ligands provide a hydrophobic shell which protects the active metal core from poisoning by larger substrates.[3] Finally, some

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(4) Reagent grade pyridine was vacuum distilled from CaO and then from a small amount of Na. Distilled water was added to this dried pyridine to give a solution which was 0.1 M in H_2O. This solution was used in the catalysis reactions.

(5) The mole percents of H_2, HD, and D_2 were determined by mass spectroscopy. The instrument used was a Leybold Inficon Quadrex 200 RGA which was tuned and calibrated in the mass 1-10 range. The peak heights were calibrated with gas mixtures of known composition.

(6) The mole percents of H_2, HD, and D_2 at equilibrium depend not only on the initial amounts of D_2 and H_2O but also on the equilibrium constants for all reactions between gaseous $(H,D)_2$ and liquid $(H,D)_2O$. There are significant isotope effects here. For example, K for the reaction $H_2O(l) + HD(g) = HDO(l) + H_2(g)$ is 3.9 at 25 °C, thus showing that the (H/D) ratio will be greater in the gas phase relative to the liquid phase. This is well-known and is the basis of many isotope separation procedures (*Separation of Hydrogen Isotopes*; Rae, H. K., Ed.; ACS Symposium Series 68; American Chemical Society: Washington, DC, 1978).

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Table 1. Rate of D_2/ROH and D_2/H_2O Exchange Reactions for Various Catalysts under Homogeneous Conditions

catalyst	reactants	obsd product	turnover rate, min^{-1}	solvent/promoter	ref
$Ru(OEP)(THF)(\eta^2\text{-}H_2)^a$	$H_2 + D_2O$ (0.1 M)[f]	HD, D_2	0.02	THF/KOD (0.1 M)	7a
$W(CO)_3(P\text{-}i\text{-}Pr_3)_2(\eta^2\text{-}D_2)$	$D_2 + H_2O$ (0.04 M)[g]	HD, H_2	ca. 1 × 10^{-4}	THF/none	7b
$[Pt(AuPPh_3)_8]^{2+}$	$D_2 + H_2O$ (0.1 M)[g]	HD, H_2	1.5[j]	pyridine/none	this work
$RhCl(PPh_3)_3$	D_2 + *t*-BuOH (1 M)[g]	*t*-BuOD	0	CH_2Cl_2/none	7c
$[CpRu(CO)(PPh_3)(\eta^2\text{-}H_2)]^+$	D_2 + *t*-BuOH (1 M)[g]	*t*-BuOD	0.1	CH_2Cl_2/none	7c
$[Ru(dppe)_2(H)(\eta^2\text{-}H_2)]^+$	D_2 + *t*-BuOH (1 M)[g]	*t*-BuOD	2	CH_2Cl_2/none	7c
$[Ir(bq)(PPh_3)_2H(\eta^2\text{-}H_2)]^{+\,b}$	D_2 + *t*-BuOH (1 M)[g]	*t*-BuOD	27	CH_2Cl_2/none	7c
$[Ni(SNO)_2]^{2+\,c}$	D_2 + EtOH (2 M)[g]	EtOD	2	DMSO/HBF_4	7d
$Rh(H)(CO)(^{bu}S_4)^d$	D_2 + EtOH (0.8 M)[h]	EtOD	5 × 10^{-3}	THF/HCl (0.04 M)	7e
$H_2PtCl_6/SnCl_2{}^e$	D_2 + MeOH (neet)[i]	HD, H_2	ca. 7 × 10^{-3}	MeOH/none	7f

[a] OEP = octaethylporphyrin. [b] bq = 7,8-benzoquinolinato. [c] SNO = *o*-$C_6H_4(OH)CH{=}N{-}NHCSNH_2$. [d] $^{bu}S_4$ = ((2-mercapto-3,5-di-*tert*-butylphenyl)thio)ethanato. [e] Mixture prepared in situ, rate reported for optimum Sn/Pt ratio. [f] $P(H_2)$ = 0.1 atm, 50 °C. [g] 1 atm pressure and ambient temp. [h] 10 atm pressure. [i] $P(D_2)$ = 25 Torr, 20 °C. [j] Rate determined for decrease in D_2 concentration for the first hour of reaction where the change in concentration with time is linear.

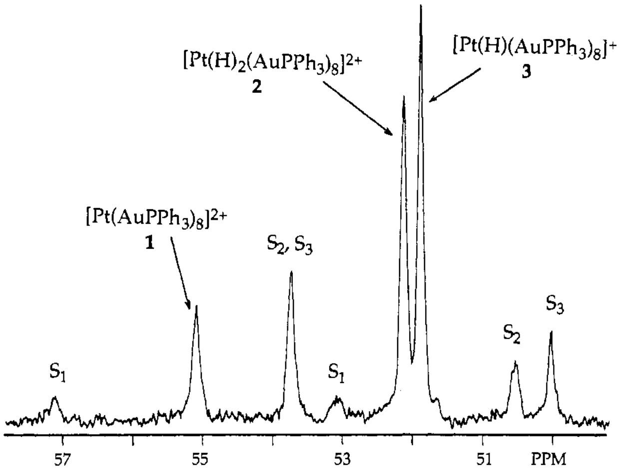

Figure 2. $^{31}P\{^1H\}$ NMR spectrum of $[Pt(AuPPh_3)_8](NO_3)_2$ (3 × 10^{-3} M) in pyridine sloution at ambient temperature under ca. 0.1 atm of H_2. The compounds were identified by their chemical shifts and coupling constants (see text and ref 11). The peaks assigned as S_1 are the ^{195}Pt satellite resonances of compound **1**, etc.

of the key cluster intermediates in the catalytic exchange reaction have been observed by NMR spectroscopy so there is the potential to completely determine the thermodynamics and kinetics (including isotope effects) of the reaction.

The $^{31}P\{^1H\}$ NMR spectrum of $[Pt(AuPPh_3)_8]^{2+}$ in pyridine solution under ca. 0.1 atm of H_2 showed a mixture of $[Pt(AuPPh_3)_8]^{2+}$, $[Pt(H)_2(AuPPh_3)_8]^{2+}$, and the monohydrido cluster compound $[Pt(H)(AuPPh_3)_8]^+$ as illustrated in Figure 2.[9] The cluster compound $[Pt(H)(AuPPh_3)_8]^+$ is not formed by the reaction of H_2 with $[Pt(AuPPh_3)_8]^{2+}$ in less basic solvents (eg, nitrobenzene, dicholormethane, acetone, or acetonitrile) where only $[Pt(H)_2(AuPPh_3)_8]^{2+}$ is observed.[3] It has been made by a different route, however, and is completely characterized.[10] The formation of these hydrido clusters was rapid and reversible. Removal of the H_2 by a N_2 purge resulted in the fast, and quantitative reformation of $[Pt(AuPPh_3)_8]^{2+}$.[11] These observations suggested that $[Pt(H)_2(AuPPh_3)_8]^{2+}$ was reversibly deprotonated by pyridine giving the mono-hydrido cluster $[Pt(H)(AuPPh_3)_8]^+$, as shown in reaction 2, which was too small for detection by NMR spectroscopy at the higher partial pressures of H_2.

$$[Pt(H)_2(AuPPh_3)_3]^{2+} + Py \rightleftarrows [Pt(H)(AuPPh_3)_8]^+ + HPy^+ \quad (2)$$

A reasonable mechanism for the $(D_2)_g/(H_2O)_l$ exchange reaction with $[Pt(AuPPh_3)_8]^{2+} = M^{2+}$ as the catalyst involves the steps shown in Scheme 1. Only steps Ia–Ic are needed to achieve isotope exchange if one permits the H and D to be interchanged in the formulas and ignores kinetic isotope effects. The production of H_2 would result from $M(H)_2{}^{2+}$, which is formed by further exchange of $M(H)(D)^{2+}$ with H_2O by steps like Ib–Id. The gas composition with time plot for the reaction of D_2 with H_2O (Figure 1) showed that H_2 was initially formed at a faster rate than HD, even though at equilibrium the concentration of HD is greater than that of H_2. This observation indicates that steps Ib and Ic occur at faster rates than step Ia. Thus the isotopic composition of the dihydrido species $M(H,D)_2{}^{2+}$ will be close to the composition in the liquid $(H,D)_2O$ phase, producing gas species of the same isotopic composition via the slower step Ia. The notation $(H,D)_2O$ refers to the three isotopic possibilites H_2O, HDO, and D_2O. In the catalytic reaction shown in Figure 1, the initial liquid phase is H_2O, giving $M(H)_2{}^{2+}$ as the major species. This results in H_2 as the major initial gas phase product as observed. The rate of HD formation will increase relative to that of H_2 as the amount of D increases in the liquid water phase, and so on to equilibrium. The final equilibrium distribution of D between the liquid and gas phases will be dictated by the equilibrium constants of the reactions between the liquid $(H,D)_2O$ and gaseous $(H,D)_2$ species.

Scheme 1

etc.

$$M^{2+} + D_2 \rightleftarrows M(D)_2{}^{2+} \text{ (slow)} \qquad \text{(Ia)}$$

$$M(D)_2{}^{2+} + Py \rightleftarrows MD^+ + DPy^+ \qquad \text{(Ib)}$$

$$DPy^+ + H_2O \rightleftarrows HPy^+ + HDO \qquad \text{(Ic)}$$

$$HPy^+ + MD^+ \rightleftarrows M(H)(D)^{2+} + Py \qquad \text{(Id)}$$

$$M(H)(D)^{2+} \rightleftarrows HD + M^{2+} \text{ (slow)} \qquad \text{(Ie)}$$

Although Scheme 1 qualitatively explains the isotope exchange results shown in Figure 1, there are other steps possible. For example, $M(H)^+$ could directly react with D_2, forming the trihydrido species $M(D)_2(H)^+$. The reverse reaction would

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(9) NMR samples at partial pressures of H_2 lower than 1 atm were prepared by introducing H_2–Ar mixtures at a total pressure of 1 atm into an evacuated NMR tube that contained the sample and sealing with use of a J. Young valve. This procedure was carried out at ambient temperature after previously degassing the sample with two freeze–pump–thaw cycles.

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(11) All of the cluster species observed in these NMR spectra have been previously characterized.[2,3,10] Their identity in pyridine solution was confirmed by comparison of ^{31}P chemical shift, δ, and ^{31}P–^{195}Pt coupling constant, *J*, values. The δ (vs TMP) and *J* values in pyridine solution were as follows: $[Pt(AuPPh_3)_8]^{2+}$, 55.0 ppm, 496 Hz; $[Pt(H)(AuPPh_3)_8]^+$, 51.5 ppm, 453 Hz; and $[Pt(H)_2(AuPPh_3)_8]^{2+}$, 52.1 ppm, 385 Hz. The δ and *J* values previously reported with CH_2Cl_2 as solvent are 55.4 ppm, 497 Hz; 52.1 ppm, 452 Hz; and 51.5 ppm, 380 Hz; respectively.

produce HD gas. Such intermediates have not been observed but are similar to ones proposed in the H_2/D_2 equilibration with monohydrido catalysts such as $[Pt(H)(PPh_3)(AuPPh_3)_7]^{2+}$.[3] We believe this step is less likely as it would lead to a faster initial production of HD, however, it could be occurring at a slower rate. More detailed kinetic experiments are in progress which should help sort out these mechanistic details.

A surprising property of $[Pt(AuPPh_3)_8]^{2+}$ is its rapid, reversible reaction with H_2 to form the dihydride complex $[Pt(H)_2(AuPPh_3)_8]^{2+}$ (reaction 1). This fast exchange is very unusual for a compound in which the hydrogen ligands are bound as classical hydrides. Such fast exchange implies η^2-H_2 bonding component;[7,12] however, little is known about the exchange properties of cluster bound, bridging hydrides. Indeed, reaction 1 is the only known example of a simple, reversible reaction between H_2 and a metal cluster compound.[13]

There is a need to develop catalysts for the isotopic exchange between hydrogen and liquid water. Important applications include the production of heavy water and the removal of tritium from contaminated water.[13] The current commercial process for the separation of deuterium from natural abundance water uses a $(H_2O)_l/(H_2S)_g$ exchange process (GS process). The primary advantage of this process is that it does not require a catalyst. The GS process has major disadvantages: (a) it requires a large volume of water and gas flow (a very large plant is required), (b) it has a low D recovery, and (c) it uses highly toxic and corrosive chemicals.[13] The development of a $(H_2O)_l/(H_2)_g$ exchange system would have many benefits including a much higher isotope separation factor, higher D recovery (19% for the GS process and 70% for the $(H_2O)_l/(H_2)_g$ exchange system), a system volume of only 4% of the $(H_2O)_l/(H_2S)_g$ system volume for the same production of heavy water, and the use of an environmentally safe, nonpolluting system. The major draw back of the $(H_2O)_l/(H_2)_g$ exchange system is that it requires a catalyst that can operate efficiently in the presence of liquid water. Although some Pt-based, heterogeneous systems have been developed (e.g. Pt on porous polytetrafluoroethylene or on alumina coated with a silicone polymer to provide a protective hydrophobic environment), there is a need for better catalysts that have high exchange rates, good stability, and can tolerate water.[13b] These Pt–Au clusters provide an interesting system to study for the possible development of a practical catalyst system.

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