Dihydrogen Activation by Mixed Platinum- and Palladium-Gold Cluster Compounds. Homogeneous Catalytic H₂-D₂ Equilibration

Mark A. Aubart, Bert D. Chandler, Rachael A. T. Gould, Don A. Krogstad, Marcel F. J. Schoondergang, and Louis H. Pignolet*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received April 27, 1994⊛

A series of Pt–Au and related phosphine-stabilized cluster compounds have been shown to be excellent catalysts for H₂–D₂ equilibration (H₂ + D₂ = 2HD) under homogeneous and heterogeneous conditions. H₂–D₂ equilibration is a model reaction for catalytic H₂ activation. Turnover rates for HD production (ca. 5 s⁻¹ for the best catalyst) were comparable to those of activated Pt surfaces. Kinetic data measured under homogeneous conditions (nitrobenzene solvent, 30 °C, 1 atm) showed the following trends in rate: (i) Faster rates were observed as the Au/Pt ratio increased. (ii) Pt–Au clusters gave faster rates than Pd–Au clusters; Au clusters were inactive. (iii) Sixteen-electron clusters were more active than 18-electron clusters; 18-electron hydrido clusters were also very active. These trends suggested that the M–Au bonds may function as active sites for H₂ activation (μ_2-H and μ_3-H bonding occurs in known hydrido clusters) with Pt–Au bonds being more active than Pd–Au bonds. The mechanism for the homogeneous, catalytic H₂–D₂ equilibration was studied by spectroscopic and kinetic measurements. For the 16-electron cluster [Pt(AuPPh₃)₈](NO₃)₂ = M, it is thought to involve the following steps: (1) M + H₂ = M(H)₂; (2) M(H)₂ = M*(H)₂ + PPh₃; (3) M*(H)₂ + D₂ = M*(H)₂(D)₂. Step 1 is directly observable by NMR spectroscopy, while steps 2 and 3 were implicated by kinetic studies as a function of H₂, D₂, and metal cluster concentration and by the effect of added PPh₃. Step 3, the formation of a 20-electron, tetra(hydrido, deuterio) species, is rate limiting and its reverse leads to HD production. The mechanism with the hydrido, 18-electron cluster [Pt(H)(PPh₃)(AuPPh₃)₇](NO₃)₂ is also thought to involve PPh₃ dissociation followed by the rate-limiting addition of D₂ giving a 20-electron, trihydrido species or activated complex. The 20-electron species have not been directly observed. These phosphine-stabilized clusters have deep and narrow hydrophobic channels into the metal core which prevents binding of many larger substrates thus protecting the core from poisoning. This helps explain the high turnover rates for HD production observed with molecular solids of these clusters. This study has shown that phosphine-stabilized, mixed-metal cluster compounds are useful as models for polymetallic surface catalysts and that structure–reactivity relations have relevance to this important area in catalysis.

Introduction

Phosphine-stabilized, platinum–gold cluster compounds have recently been reported to be very active catalysts for the H₂–D₂ equilibration reaction (H₂ + D₂ = 2HD).[1] For example, [Pt(AuPPh₃)₈](NO₃)₂ (PPh₃ = triphenylphosphine) exhibits turnover rates for HD production of 0.075 and ca. 5 s⁻¹, respectively, under homogeneous (nitrobenzene solution) and heterogeneous (molecular solid–gas) conditions (1 atm, 30 °C).[1,2] These rates are among the fastest reported thus far for any molecular compound, and the activity of the crystalline molecular solid is comparable to that of activated Pt surfaces. Importantly, these cluster compounds catalyze H₂–D₂ equilibration *without any H/D exchange* with solvent, water, ethanol, or ligand hydrogen atoms.[1] This is contrary to results reported for many monometallic systems where hydrogen exchange between metal hydrides and solvents or ligands is common.[3] These clusters are therefore unusual in that they show clean H₂–D₂ equilibration at the metal core. Bi-

and polymetallic clusters of this type therefore have potential to serve as *models* for the activation of H₂ by supported Pt–Au and Pd–Au catalysts. This is important because it is known that the addition of gold to heterogeneous platinum and palladium catalysts has significant effects on activity and selectivity.[4] Supported bimetallic catalysts are difficult to study, and the mechanism by which gold alters their selectivity and activity is not well understood.[4] It is anticipated that the study of a wide variety of ligand-stabilized, M–Au cluster compounds of known molecular structure will help in understanding how gold affects the reactivity of supported bimetallic catalysts.[5]

We have available for study a large variety of bi- and trimetallic cluster compounds of known molecular structure. For example, some recently characterized clusters, in addition to [Pt(AuPPh₃)₈](NO₃)₂, are [Pd(AuPPh₃)₈](NO₃)₂,[6] [Pt(PPh₃)(AuPPh₃)₆](NO₃)₂,[7] [Pt(H)(PPh₃)(AuPPh₃)₇](NO₃)₂,[8] [Pt(CO)(AuPPh₃)₈]-

⊛ Abstract published in *Advance ACS Abstracts*, July 15, 1994.
(1) Aubart, M. A.; Pignolet, L. H. *J. Am. Chem. Soc.* **1992**, *114*, 7901.
(2) Kappen, T. G. M. M.; Bour, J. J.; Schlebos, P. P. J.; Roelofsen, A. M.; van der Linden, J. G. M.; Steggerda, J. J.; Aubart, M. A.; Krogstad, D. A.; Schoondergang, M. F. J.; Pignolet, L. H. *Inorg. Chem.* **1993**, *32*, 1074.
(3) See for example: (a) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913. (b) Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1. (c) Albeniz, A. C.; Heinekey, D. M.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 3632. (d) Carr, S. W.; Fowles, E. H.; Fontaine, X. L. R.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1990**, 573. (e) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824. (f) Anderson, G. K.; Saum, S. E.; Cross, R. J.; Morris, S. A. *Organometallics* **1983**, *2*, 280. Parshall, G. *J. Am. Chem. Soc.* **1968**, *90*, 1669. James, B. R. *Homogeneous Hydrogenations*; Wiley-Interscience: New York, 1973.

(4) See for example: (a) Schwank, J.; Balakrishnan, K.; Sachdev, A. In *New Frontiers in Catalysis*; Guczi, L., Solymosi, F., Tetenyi, P., Eds; Elsevier: Amsterdam, 1993; p 905. (b) Rouabah, D.; Fraissard, J. *J. Catal.* **1993**, *144*, 30. (c) Balakrishnan, K.; Schwank, J. *J. Catal.* **1991**, *132*, 451. (d) Sachdev, A.; Schwank, J. *J. Catal.* **1989**, *120*, 353. (e) Sermon, P. A.; Thomas, J. M.; Keryou, K.; Millward, G. R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 918. (f) Balakrishnan, K.; Sachdev, A.; Schwank, J. *J. Catal.* **1990**, *121*, 441. (g) Yates, R. C.; Somorjai, G. A. *J. Catal.* **1987**, *103*, 208. (h) Sinfelt, J. H. *Bimetallic Catalysts*; Wiley: New York, 1985. (i) Clarke, J. K. A.; Manninger, L.; Baird, T. *J. Catal.* **1978**, *54*, 230.
(5) Braunstein, P.; Rose, J. In *Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: Amsterdam, 1988; Vol. 3, Chapter 1, p 3. Braunstein, P.; Rose, J. *Gold Bull.* **1985**, *18*, 17. Suss-fink, G.; Meister, G. *Adv. Organomet. Chem.* **1993**, *35*, 41. *Studies in Surface Science and Catalysis*; Gates, B. C., Guczi, L., Knözinger, H., Eds.; Elsevier: Amsterdam, 1986; Vol. 29 and references cited therein. Ichikawa, M. *Adv. Catal.* **1992**, *38*, 283.

$(NO_3)_2,$[9] $[Pt(MX)(AuPPh_3)_8](NO_3)_2$, where MX = $AgNO_3$[10] or $CuCl,$[11] $[Pt(HgNO_3)_2(AuPPh_3)_8](NO_3)_2,$[12] and the supracluster $[Pt_2(AuPPh_3)_{10}Ag_{13}Cl_7].$[13] Structural and reactivity properties of this general class of cluster compounds have been rationalized with the use of electron counting rules.[14-16] For example, 16-electron clusters have a flattened, toroidal geometry and react with 2-electron donors to give 18-electron clusters with spheroidal geometry. An example is the reaction of the Pt- and Pd-centered, 16-electron clusters $[M(AuPPh_3)_8]^{2+}$ with CO to give the spheroidal 18-electron clusters $[M(CO)(AuPPh_3)_8]^{2+}$ (see Figure 1).[15] Most of the structures of the 18-electron, spheroidal clusters can be described as metal-centered, icosahedral fragments, although distorted cubes are also known.[8,17,18]

$[Pt(AuPPh_3)_8](NO_3)_2$ has been shown to rapidly and *reversibly* react with H_2 in solution and in the solid state according to eq 1.[2] In the solid ca. 0.9 mol equiv of H_2 is reversibly taken up at

$$[Pt(AuPPh_3)_8](NO_3)_2 + H_2 \rightleftharpoons [Pt(H)_2(AuPPh_3)_8](NO_3)_2 \quad (1)$$
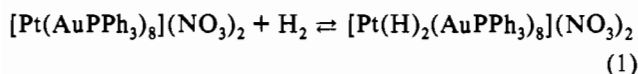
1 atm pressure and 25 °C. Although the structure of the 18-electron cluster $[Pt(H)_2(AuPPh_3)_8](NO_3)_2$ has not been determined by X-ray diffraction, NMR data (CH_2Cl_2 solution) including T_1 measurements of the metal-bound hydrogen ligands clearly show its classical, dihydrido nature.[2] $[Pt(H)_2(AuPPh_3)_8]$-$(NO_3)_2$ is of obvious importance in the H_2–D_2 equilibration reaction as it is likely to be an intermediate in the catalytic process (vide infra).

In this paper we report the details of the homogeneous, catalytic H_2–D_2 equilibration reaction for a series of well-characterized Pt–Au cluster compounds, in addition to several other M–Au (M = Pd and Au) and trimetallic clusters. We also report the results of a study on the mechanism of this catalytic reaction. This is the first study of the kinetics of H_2–D_2 equilibration with metal cluster compounds under homogeneous conditions.[19] There have been numerous studies of this reaction under heterogeneous conditions (activated metal surfaces and supported metals)[20-23] where it is difficult to measure specific rates and determine reaction mechanisms. A study under homogeneous conditions offers an advantage in determining reaction mechanism. Previous kinetic studies under homogeneous conditions have included
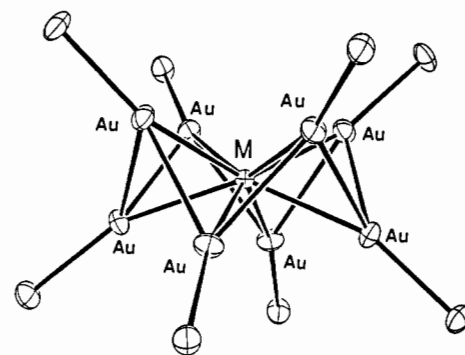
$[M(AuPPh_3)_8]^{2+}$
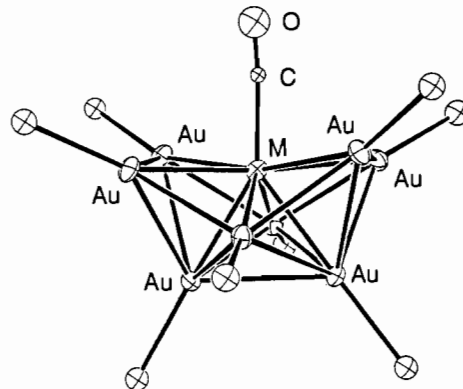
$[M(CO)(AuPPh_3)_8]^{2+}$

Figure 1. Structures of the 16-electron, $[M(AuPPh_3)_8]^{2+}$ cluster (M = Pt or Pd) and the 18-electron, CO adduct $[M(CO)(AuPPh_3)_8]^{2+}$ showing the change from flattened, toroidal geometry to spheroidal geometry. A triphenylphosphine P atom is bonded to each Au atom. The Pt and Pd centered clusters have nearly identical structures.

monometallic compounds such as *trans*-$IrCl(CO)(PPh_3)_2,$[24] $Pt(O_2)(PPh_3)_2,$[24] $NiI_2(PPh_3)_2,$[25] $RhCl(PPh_3)_3,$[26] $RuH_2(PPh_3)_4,$[27] and $RuHCl(PPh_3)_3.$[27]

Results and Discussion

Rate Studies of Catalytic H_2–D_2 Equilibration. (i) Homogeneous Solution Conditions. The rates for the catalytic production of HD from an equimolar mixture of H_2 and D_2 (1 atm pressure, 30 °C) have been determined for a series of M–Au cluster compounds (M = Pt, Pd, Au) under homogeneous conditions with use of nitrobenzene as solvent. The rates are reported as turnover rates with units (mol of HD)(mol of cluster)$^{-1}$(s)$^{-1}$ and range from 0.22 s^{-1} for $\{Pt[AuP(p\text{-tolyl})_3]_8\}(NO_3)_2$ to zero for $[Au(AuPPh_3)_8](NO_3)_3$ (P(p-tolyl)$_3$ = tri-p-tolylphosphine). Rate data for all of the compounds studied with nitrobenzene as solvent

(6) Ito, L. N.; Johnson, B. J.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1989**, *28*, 2026.

(7) Ito, L. N.; Sweet, J. D.; Mueting, A. M.; Pignolet, L. H.; Schoondergang, M. F. J.; Steggerda, J. J. *Inorg. Chem.* **1989**, *28*, 3696.

(8) Kanters, R. P. F.; Bour, J. J.; Schlebos, P. P. S.; Behm, H.; Steggerda, J. J.; Ito, L. N.; Pignolet, L. H. *Inorg. Chem.* **1989**, *28*, 2591.

(9) Kanters, R. P. F.; Schlebos, P. P. J.; Bour, J. J.; Bosman, W. P.; Behm, H. J.; Steggerda, J. J. *Inorg. Chem.* **1988**, *27*, 4034.

(10) Kanters, R. P. F.; Schlebos, P. P. J.; Bour, J. J.; Bosman, W. P.; Smits, J. M. M.; Beurskens, P. T.; Steggerda, J. J. *Inorg. Chem.* **1990**, *29*, 324.

(11) Schoondergang, M. F. J.; Bour, J. J.; Schlebos, P. P. J.; Vermeer, A. W. P.; Bosman, W. P.; Smits, J. M. M.; Beurskens, P. T.; Steggerda, J. J. *Inorg. Chem.* **1991**, *30*, 4704.

(12) Bour, J. J.; Berg, W. v. d.; Schlebos, P. P.; Kanters, R. P. F.; Schoondergang, M. F. J.; Bosman, W. P.; Smits, J. M. M.; Beurskens, P. T.; Steggerda, J. J.; van der Sluis, P. *Inorg. Chem.* **1990**, *29*, 2971.

(13) This cluster has been prepared by the Steggerda research group (Kappen, T. G. M. M.; Schlebos, P. P. J.; Bour, J. J.; Bosman, W. P.; Smits, J. M. M.; Beurskens, P. T.; Steggerda, J. J. *Inorg. Chem.* **1994**, *33*, 754) and has a similar structure to $[PtAu(AuPPh_3)_{11}Ag_{12}Cl_7]Cl$ recently reported by Teo (Teo, B. K.; Zhang, H.; Shi, X. *J. Am. Chem. Soc.* **1993**, *115*, 8489).

(14) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall: Englewood Cliffs, NJ, 1993. Mingos, D. M. P.; Johnston, R. L. *Struct. Bonding* **1987**, *68*, 29. Stone, A. J. *Inorg. Chem.* **1981**, *20*, 563. Steggerda, J. J. *Comments Inorg. Chem.* **1991**, *11*, 113.

(15) Ito, L. N.; Felicissimo, A. M. P.; Pignolet, L. H. *Inorg. Chem.* **1991**, *30*, 387.

(16) Kanters, R. P. F.; Schlebos, P. P. J.; Bour, J. J.; Bosman, W. P.; Smits, J. M. M.; Beurskens, P. T.; Steggerda, J. J. *Inorg. Chem.* **1990**, *29*, 324.

(17) Gould, R. A. T.; Pignolet, L. H. *Inorg. Chem.* **1994**, *33*, 40.

(18) Smith, E. W.; Welch, A. J.; Treurnicht, I.; Puddephatt, R. J. *Inorg. Chem.* **1986**, *25*, 4616.

(19) The only other homogeneous study we could find was on the photoinduced equilibration by $H_4Ru_4(CO)_{12}$, but no rate data were reported: Doi, Y.; Tamura, S.; Koshizuka, K. *J. Mol. Catal.* **1983**, *19*, 213.

(20) See for example: Sekine, R.; Iwasawa, Y. *J. Mol. Catal.* **1993**, *78*, 327. Jen, H-W.; Brenner, A. In *Proceedings of the Vth International Symposium on Relations between Homogeneous and Heterogeneous Catalysis*; Novosibirsk, USSR; Yermakov, Y., Likholobov, V., Eds.; VNU Science Press: Utrecht, The Netherlands, 1986; p 865. Tanaka, K.; Watters, K. L.; Howe, R. F.; Andersson, S. L. T. *J. Catal.* **1983**, *79*, 251. Breakspere, R. J.; Eley, D. D.; Norton, P. R. *J. Catal.* **1972**, *27*, 215.

(21) Burden, A. G.; Grant, J.; Martos, J.; Moyes, R. B.; Wells, P. B. *Faraday Disc. Chem. Soc.* **1982**, *72*, 95.

(22) Bond, G. C. *Catalysis by Metals*; Academic Press: New York, 1962; Chapter 8.

(23) Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell Univ. Press: Ithaca, NY, 1981.

(24) Tadros, M. E.; Vaska, L. *J. Colloid Interface Sci.* **1982**, *85*, 389.

(25) Ando, N.; Maruya, K.-I.; Mizoroki, T.; Ozaki, A. *J. Catal.* **1971**, *20*, 299.

(26) Strathdee, G.; Given, R. *Can. J. Chem.* **1974**, *52*, 2216 and 2226. Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711.

(27) Strathdee, G.; Given, R. *Can. J. Chem.* **1975**, *53*, 106.

Table 1. Rate Data for Catalytic H_2-D_2 Equilibration under Homogeneous Conditions[a]

| compd	turnover rate $\times 10^2$ (s^{-1}) for HD production
16-Electron Compounds	
{Pt[AuP(p-tolyl)$_3$]$_8$}(NO$_3$)$_2$	22
[Pt(AuPPh$_3$)$_8$](NO$_3$)$_2$[b]	7.5
[Pt(PPh$_3$)(AuPPh$_3$)$_6$](NO$_3$)$_2$[c]	2.1
[Pt(PPh$_3$)$_2$(AuPPh$_3$)$_3$]NO$_3$[d]	4.2
[Pd(AuPPh$_3$)$_8$](NO$_3$)$_2$[e]	0.10
[Au(AuPPh$_3$)$_8$](NO$_3$)$_3$[f]	0
Pt(C$_2$H$_4$)(PPh$_3$)$_2$[g]	0.11
trans-IrCl(CO)(PPh$_3$)$_2$[h]	0.15
18-Electron Compounds	
[Pt(CO)(AuPPh$_3$)$_8$](NO$_3$)$_2$[i]	0.71
[Pt(RNC)(AuPPh$_3$)$_8$](NO$_3$)$_2$[j]	0.20
[Pt(PPh$_3$)(AuPPh$_3$)$_7$]NO$_3$[k]	0.16
[Pt$_3$Au(μ-CO)$_3$(PPh$_3$)$_5$]NO$_3$[l]	0.3
18-Electron Hydrido Compounds	
[Pt(H)(PPh$_3$)(AuPPh$_3$)$_7$](NO$_3$)$_2$[m]	7.7
[Pt(H)(PPh$_3$)(AuPPh$_3$)$_6$]NO$_3$[n]	2.1
Trimetallic Compounds	
[Pt(CuCl)(AuPPh$_3$)$_8$](NO$_3$)$_2$[o]	15
[Pt(AgNO$_3$)(AuPPh$_3$)$_8$](NO$_3$)$_2$[p]	4.0
[Pt(H)(AgNO$_3$)(AuPPh$_3$)$_8$]NO$_3$[q]	4.4
[(PPh$_3$)Pt(HgNO$_3$)(AuPPh$_3$)$_6$]NO$_3$[r]	0.60
Pt$_2$(AuPPh$_3$)$_{10}$Ag$_{13}$Cl$_7$[s]	0

[a] Turnover rates were determined as described in the Experimental Section. The experimental error in turnover rate is estimated to be ±5%. Values reported are averages of at least two determinations. Compound concentrations in the range (2.5–6.4) $\times 10^{-4}$ M with nitrobenzene as solvent, initial H_2 + D_2 partial pressure of 760 Torr, and 30 °C. The compounds were prepared from the literature references given below. [b] Reference 41. [c] Reference 7. [d] Reference 15. [e] Reference 6; the value is slightly lower than previously reported in ref 2. [f] Reference 49; no HD observed after 2 days. [g] Reference 49. [h] Reference 24. [i] Reference 9. [j] Reference 50 and R = 2,6-dimethylphenyl. [k] Reference 51. [l] Reference 52. [m] Reference 8. [n] Reference 37. [o] Reference 11; reacts with H_2 to irreversibly form the 18-electron monohydride [Pt(H)(CuCl)(AuP-Ph$_3$)$_8$]NO$_3$ (see text). [p] Reference 10. [q] Reference 35. [r] Reference 17. [s] Reference 13; no HD observed after 1 day.

are reported in Table 1 (refer to the Experimental Section and Figures 2 and 3 for details of the rate measurements). Rates for some cluster compounds were also determined with use of acetonitrile as solvent and will be discussed later. The cluster compounds listed in the table are sorted by electron count (16 and 18) and by composition (hydrido and trimetallic) as this simplifies a discussion of the results. Rate data for several monometallic compounds are also listed for comparison. It is important to emphasize that the catalytic production of HD in nitrobenzene solution is a true homogeneous reaction and is *not* caused by solid impurities or irreversible cluster decomposition to colloidal metal. The rates are also not limited by gas–solution diffusion because they are first-order in cluster concentration for the concentration range reported (vide infra). Numerous control experiments have been carried out to demonstrate the homogeneous nature of this reaction. The results of these controls are reported below.

Some general trends are apparent from the rate data shown in Table 1. Sixteen-electron clusters gave faster turnover rates than non-hydrido 18-electron clusters, but hydrido 18-electron clusters showed rates that were similar to their 16-electron non-hydrido analogues. The effect on rate of the central metal in MAu$_8$ clusters was pronounced with Pt $\gg$ Pd $\gg$ Au. Sixteen-electron, platinum-centered clusters with the larger number of Au or Cu atoms generally gave faster turnover rates as evidenced by the order PtCuAu$_8$ > PtAu$_8$ > PtAu$_6$ > PtAu$_0$ (PtAu$_3$ > PtAu$_6$ is the only exception). This trend was also followed with 18-electron, hydrido clusters, where [Pt(H)(PPh$_3$)(AuPPh$_3$)$_7$]-(NO$_3$)$_2$ gave a faster turnover rate than [Pt(H)(PPh$_3$)(AuPPh$_3$)$_6$]-NO$_3$. The very stable, 18-electron supracluster was inactive for
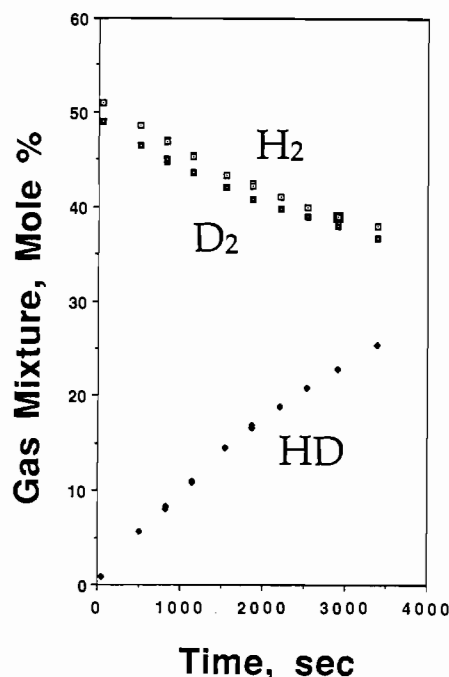
Figure 2. Typical reaction profile for H_2-D_2 equilibration with the catalyst [Pt(AuPPh$_3$)$_8$](NO$_3$)$_2$. Reaction conditions are as described in the Experimental Section with cluster concentration = 6.4 $\times 10^{-4}$ M in nitrobenzene solution, (H,D)$_2$ pressure = 760 Torr, and T = 30 °C.
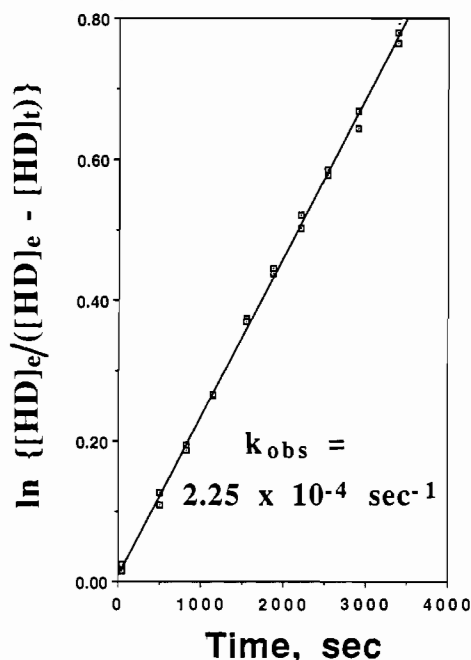
Figure 3. Kinetic plot for HD production from the data in Figure 1. [HD]$_e$ and [HD]$_t$ are the mole fractions of HD at equilibrium and at time t, respectively. The observed rate constant, k_{obs}, in s^{-1} equals the slope of the line as described in the Experimental Section.

H_2-D_2 equilibration. The presence of silver in Pt–Au clusters is less effective in activating H_2 than copper; however, this is based on only one comparison. The cluster {Pt[AuP(p-tolyl)$_3$]$_8$}(NO$_3$)$_2$ gave a 3-fold increase in turnover rate compared with its triphenylphosphine analogue. This showed that a more electron-rich cluster is more reactive for H_2 activation, in agreement with general observations from metal hydride chemistry.[3] Finally, the 16-electron, coordinatively unsaturated compound Pt(C$_2$H$_4$)-(PPh$_3$)$_2$ was more than 1 order of magnitude *less* active for H_2-D_2 equilibration than the 16-electron Pt–Au cluster compounds. The above trends and implications have been determined from the results of solution rate data. Since the H_2-D_2 equilibration

reaction is complex mechanistically (two bonds must be broken and H/D scrambling must occur), some of these trends could result from differences in reaction mechanism for the various catalysts (vide infra).

(ii) Heterogeneous (Molecular Solid–Gas) Conditions. Several of the cluster compounds were also excellent catalysts for H_2–D_2 equilibration in the solid state (gas–molecular solid reaction) with turnover rates of ca. 5 and 2 s^{-1} for powdered samples of $[Pt(AuPPh_3)_8](NO_3)_2$ and $[Pt(PPh_3)(AuPPh_3)_6](NO_3)_2$, respectively, at 1 atm pressure and 30 °C. In the calculation of these turnover rates it was assumed that all cluster molecules in the solid samples were active. These rates are significantly greater than under homogeneous solution conditions and are comparable to rates observed for activated Pt surfaces.[20–23] There was a marked dependence on surface area, however, making meaningful comparisons between samples unreliable. The greatest rates were observed with finely divided powders prepared by fast precipitation from solution. This surface area effect on rate was most likely caused by gas diffusion into the solid, crystalline materials. In suport of this, we have obtained reproducible, fast rates with clusters supported on the surface of alumina particles (60–80 mesh, 86 m^2/g surface area). In addition, powdered samples of $[Pt(AuPPh_3)_8](NO_3)_2$ *slowly* adsorbed ca. 0.9 mol equiv of H_2 (equilibrium reached in ca. 15 min), while the same amount of H_2 was *rapidly* adsorbed (<20 s) by the cluster supported on alumina.[28]

It must be considered that the solid-state H_2–D_2 equilibration was caused by a small amount of metallic platinum impurity. This was unlikely, however, because a mixture of 20 mg of crystalline $[Pt(AuPPh_3)_8](NO_3)_2$ with 0.5 atm of D_2 and 0.5 atm of C_2H_4 gave no evidence of H/D exchange or hydrogenation (GC and MS analysis) after several days at 25 °C. Metallic platinum is a good catalyst for H/D exchange and hydrogenation of ethylene, and its presence would be expected to show significant reactivity.[29] We did observe some hydrogenation of ethylene by large (100 mg) solid samples of $[Pt(AuPPh_3)_8](NO_3)_2$, but the turnover rate was more than 4 orders of magnitude slower than that observed for H_2–D_2 equilibration.[2] The turnover rates for H_2–D_2 equilibration with these molecular clusters were also too high to be reasonably caused by an undetectable metallic Pt impurity or cluster fragmentation product (vide infra).

To our knowledge, this H_2–D_2 equilibration reaction has not previously been reported for any solid, molecular, metal compound with non-volatile ligands.[30] There have been several recent reports on molecular solid–gas catalytic transformations with organometallic compounds, however.[31] This general area is virtually unexplored and of obvious importance due to the high reactivity and different selectivity of some organometallic molecular solids.[31] We are currently studying these interesting solid-state reactions, and results will be reported in a future publication.

Evidence for the Homogeneous Nature of the Catalytic Reaction in Solution. A number of experiments were carried out in order to determine if the rapid H_2–D_2 equilibration observed with nitrobenzene solutions of the cluster compounds could be catalyzed

by zerovalent metal impurities or by irreversible cluster decomposition. All of the results were consistent with true homogeneous catalysis by the dissolved molecular cluster compounds. We observed no H/D exchange with solvent, ligands, or added water or ethyl alcohol. This was determined by day long experiments with use of only D_2 as the reactant gas. No HD or H_2 was produced in these experiments which were run under the usual catalysis conditions with $[Pt(AuPPh_3)_8](NO_3)_2$, $[Pt(PPh_3)(AuPPh_3)_6]$-$(NO_3)_2$, and $[Pt(H)(PPh_3)(AuPPh_3)_7]$-$(NO_3)_2$. NMR and MS analysis also indicated no deuterium incorporation into the PPh_3 ligands. In agreement with the absence of H/D exchange, the relative amounts of H_2 and D_2 decreased at the same rate during catalysis runs with all clusters (see Figure 2 as an example). This result is important because many organometallic hydride and molecular hydrogen compounds and zerovalent metal surfaces cause H/D exchange between D_2 and protic solvents such as alcohol and water.[3,22,23,29] For example, catalytic H_2–D_2 equilibration with *trans*-Ir(CO)Cl(PPh$_3$)$_2$ in toluene solvent shows a significant increase in H relative to D during the reaction.[24] The Pt–Au cluster compounds are therefore unusual in that they show clean H_2–D_2 equilibration without any H/D exchange in the solvents used in this study. The presence of catalytically active, solid metal impurities or monometallic, unsaturated Pt compounds from cluster decomposition is therefore very unlikely. For example, the unsaturated, monometallic Pt compound Pt(C$_2$H$_4$)-$(PPh_3)_2$ is a poor catalyst for H_2–D_2 equilibration, having a turnover rate that is nearly 2 orders of magnitude slower than $[Pt(AuPPh_3)_8](NO_3)_2$. In addition, nitrobenzene (chosen as the solvent because it is rapidly hydrogenated by heterogeneous, platinum metal surfaces[29] and therefore is a good internal control) is not hydrogenated to aniline nor is H_2 taken up in week long control reactions using much higher concentrations of the Pt–Au clusters. Olefins such as 1-hexene and cyclohexene are also not hydrogenated by these cluster catalysts after several days (1 atm H_2 pressure, 30 °C) in nitrobenzene or acetonitrile solvents, and ethylene is only hydrogenated very slowly[2] (vide infra). The turnover rates for H_2–D_2 equilibration are reproducible for different preparations of cluster compounds. This would not be expected if solid impurities were responsible for the catalysis. Finally, many of the catalysis reactions were checked by $^{31}P\{^1H\}$ NMR and UV–vis spectroscopy before and after the kinetic runs and no decomposition was observed. These results provide good evidence for the homogeneous nature of H_2–D_2 equilibration catalyzed by Pt–Au cluster compounds in nitrobenzene solution. Although we have not carried out such extensive controls with acetonitrile as solvent, all of our observations with this solvent led to the same conclusion.

Effects of Concentration, Solvent, and Added Ligand on the Rate of the Catalytic, Homogeneous Reaction. In order to better understand the nature of the homogeneous, catalytic H_2–D_2 equilibration, kinetic experiments were run for a variety of reaction conditions. Most of these studies were done with $[Pt(AuPPh_3)_8]$-$(NO_3)_2$ as we assume it is a typical 16-electron example. The rate of HD production was found to be first-order in cluster concentration in nitrobenzene and acetonitrile solutions in the concentration range $(2.5–6.4) \times 10^{-4}$ M. The data in the form of a $\ln(k_{obs})$ *vs* $\ln([cluster])$ plot are shown in Figure 4 for nitrobenzene solution. The slope of the straight line in this plot was 0.98, confirming the first-order dependence on cluster concentration. Similar results were obtained with $[Pt(PPh_3)$-$(AuPPh_3)_6](NO_3)_2$ and $[Pt(H)(PPh_3)(AuPPh_3)_7](NO_3)_2$ in nitrobenzene and acetonitrile solutions. This result is important because it shows that the rate of H_2 and D_2 diffusion between the solution and gas phases does not limit the rate of HD production.[32]

There was a significant solvent effect on the rate of H_2–D_2 equilibration. This is primarily due to differences in H_2 solubility (vide infra). For example, the turnover rate for HD production with acetonitrile as solvent was 36×10^{-2} s^{-1}, compared with the

(28) Studies with clusters supported on alumina are under current investigation and will be reported in a future publication.

(29) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855. Rylander, P. N. *Catalytic Hydrogenation over Platinum Metals*; Academic Press: New York, 1967; Chapter 11. Hudlicky, M. *Reductions in Organic Chemistry*; Halstead Press: New York, 1984; pp 71–76. Gudkov, B. S. *Russ. Chem. Rev.* **1986**, *55*, 259. Nazario, P.; Brenner, A. *Proc. Int. Cong. Catal., 9th* **1988**, 1020. Kemball, C. *J. Chem. Soc.* **1956**, 735. See ref. 22, Chapter 11.

(30) The only examples of this solid-state reaction we could find are for Ru$_6$C(CO)$_{17}$[21] and W(CO)$_3$(P-*i*-Pr)$_2$(H$_2$) (Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000).

(31) Bianchini, C.; Frediani, P.; Graziani, M.; Kaspar, J.; Meli, A.; Peruzzini, M.; Vizza, F. *Organometallics* **1993**, *12*, 2886. Bianchini, C.; Farnetti, E.; Graziani, M.; Kaspar, J.; Vizza, F. *J. Am. Chem. Soc.* **1993**, *115*, 1753 and references cited therein. Siedle, A. R.; Newmark, R. A. *Organometallics* **1989**, *8*, 1442.
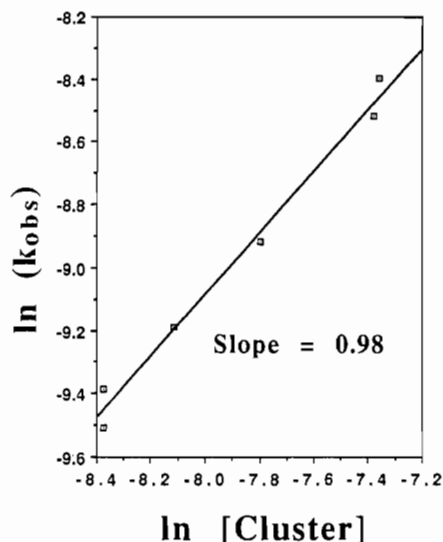
Figure 4. Rate dependence for HD production on the molar concentration of the cluster $[Pt(AuPPh_3)_8](NO_3)_2$ with constant $P_{(H,D)_2}$ showing first-order dependence. Reaction conditions are as described in the Experimental Section with solvent = nitrobenzene, cluster concentration range = $(2.5-6.4) \times 10^{-4}$ M, $(H,D)_2$ partial pressure = 760 Torr, and $T = 30$ °C. [Cluster] = [M] + [MH_2], where M = $[Pt(AuPPh_3)_8](NO_3)_2$ (see text).

Table 2. Effects of Solvent and Added Ligand on the Rate of Homogeneous, Catalytic H_2–D_2 Equilibration with $[Pt(AuPPh_3)_8](NO_3)_2$[a]

solvent (added ligand)	turnover rate $\times 10^2$ (s^{-1}) for HD production
acetonitrile	36
acetonitrile/nitrobenzene, 1:1 v/v	15
acetonitrile/toluene, 1:1 v/v	15
nitrobenzene	7.5
nitrobenzene (1 mol equiv of PPh_3)	7.8
nitrobenzene (3 mol equiv of PPh_3)	<0.1[b]
nitrobenzene (0.4 mol equiv of CO)	5.5

[a] Turnover rates were determined as described in the Experimental Section and have an estimated error of ±5%. Compound concentrations in the range $(2.5-6.4) \times 10^{-4}$ M, initial $H_2 + D_2$ partial pressure of 760 Torr, and 30 °C. [b] No HD observed for the first hour of reaction.

value of 7.5×10^{-2} observed with nitrobenzene as solvent. The solubility of H_2 in acetonitrile at 30 °C and 1 atm H_2 partial pressure (see Experimental Section) is 3.9 times greater than in nitrobenzene. These results are presented in Tables 2 and 3 and will be discussed in the section on mechanism.

The effect of added ligand L on the rate of H_2–D_2 equilibration was studied, and the results are reported in Table 2. Addition of a large molar excess of CO to a nitrobenzene solution of [Pt-(AuPPh_3)_8](NO_3)_2, followed by pumping of the excess, completely stopped the production of HD under normal catalytic conditions. This ligand is known to form the stable adduct [Pt(CO)(AuPPh_3)_8]-(NO_3)_2 and therefore prevent H_2 bonding.[9] This has been con-

firmed by $^{31}P\{^1H\}$ NMR experiments. Importantly, the addition of 0.4 mol equiv of CO to an active catalyst system of $[Pt(AuPPh_3)_8](NO_3)_2$ only weakly inhibited the rate of HD production. The addition of more than 2 mol equiv of PPh_3 to acetonitrile or nitrobenzene solutions of $[Pt(AuPPh_3)_8](NO_3)_2$ or $[Pt(H)(PPh_3)(AuPPh_3)_7](NO_3)_2$ under normal catalysis conditions significantly slowed the production of HD. However, the rate of HD production was not affected by the addition of 1 mol equiv of PPh_3. $^{31}P\{^1H\}$ NMR showed that, under 0.5 atm of H_2 with acetonitrile as solvent, the presence of 2 mol equiv of PPh_3 had no measurable effect on the position of the equilibrium of reaction 1 (Table 3) and the added PPh_3 was observed in its normal unshifted position.[33] A similar result was obtained with $[Pt(H)(PPh_3)(AuPPh_3)_7](NO_3)_2$. It was also observed that the addition of a 100 mol excess of P(p-tolyl)_3 to $[Pt(AuPPh_3)_8]$-(NO_3)_2 under a N_2 atmsphere showed no ligand substitution for at least 12 h; however, exchange did occur under 1 atm of H_2. These kinetic and NMR observations have important mechanistic implications for the catalytic H_2–D_2 equilibration reaction and will be discussed in a later section.

The effect of the H_2 and D_2 concentrations on the rate of HD production was also examined with nitrobenzene as solvent for two of the clusters, $[Pt(AuPPh_3)_8](NO_3)_2$ and $[Pt(H)(PPh_3)$-(AuPPh_3)_7](NO_3)_2. These clusters were chosen because they represent the two types of catalysts which have good activity, a 16-electron cluster and an 18-electron hydrido cluster. The initial partial pressure of $H_2 + D_2$ was varied by diluting the reactant gases with Ar as described in the Experimental Section. Equal amounts of H_2 and D_2 were used in these experiments, and the total pressure ($H_2 + D_2 + Ar$) was constant at 1 atm. The initial concentration of $H_2 + D_2$ in nitrobenzene solvent was determined experimentally at 1 atm pressure (Experimental Section). The concentrations for lower partial pressures were calculated with the assumption that the solubility of H_2 and D_2 are the same and follow Henry's law (these approximations should not lead to significant errors; see Experimental Section). Complications from solvent vapor pressure are absent because the vapor pressure of nitrobenzene is less than 1 Torr. HD production was monitored as usual, and reaction profiles and kinetic plots appeared normal and similar to the ones shown in Figures 2 and 3. The results are shown for both clusters in Table 4 and in Figure 5 by ln-(turnover rate) vs $\ln(P_{(H,D)_2})$ plots. The turnover rate is defined as (mol of HD)/(M_T)(s), where M_T is the number of moles of all cluster species. Note that the initial $[H_2] + [D_2]$ is equal to the total $[H_2] + [D_2] + [HD]$ concentration throughout the reaction if isotope effects on solubility are ignored.[34] This total concentration will hereafter be referred to as $[(H,D)_2]$ where $(H,D)_2$ represents all three isotopic possibilities. The results show that the rate of HD production has a first-order (slope = 1.0) dependence on $[(H,D)_2]$ for $[Pt(H)(PPh_3)(AuPPh_3)_7](NO_3)_2$ but that the order is greater than one for $[Pt(AuPPh_3)_8](NO_3)_2$. These results indicated that these clusters have different mechanisms and will be discussed later.

Interaction of H_2 with the Clusters. All of the clusters studied in this paper were examined for reactivity with H_2 in solution (1 atm, 25 °C) by $^{31}P\{^1H\}$ NMR. Two of the trimetallic clusters, $[Pt(AgNO_3)(AuPPh_3)_8](NO_3)_2$ and $[Pt(CuCl)(AuPPh_3)_8](NO_3)_2$,

---

(32) Note that $[Pt(AuPPh_3)_8](NO_3)_2$, M, is partly converted into $[Pt(H)_2$-(AuPPh_3)_8](NO_3)_2, MH_2, under 1 atm of H_2 (eq 1) so [cluster] in Figure 4 refers to total cluster concentration M_T = [M] + [MH_2]; however, first-order dependence is also observed for either of the individual species since $[MH_2]/[M]$ is a constant for different values of M_T (vide infra). Some deviation from first-order dependence was observed at significantly lower concentrations for both clusters in nitrobenzene and acetonitrile solutions. Solutions of the clusters which were <1 × 10^{-4} M gave rates for HD production that were greater than predicted by extrapolation of the line in Figure 4. We believe this is the effect of reversible PPh_3 dissociation. This is supported by PPh_3 inhibition experiments (vide infra). The percent of ligand dissociation would increase with dilution thereby increasing the relative amount of a more reactive species. We have been unable to detect any such species, however, by $^{31}P\{^1H\}$ NMR or UV-vis spectroscopic analysis under 1 atm H_2, so the extent of dissociation is small or the cluster product(s) difficult to observe. The kinetic data reported in Table 1 were determined with cluster concentrations in the range where first-order dependence was followed.

(33) After several hours under 1 atm of H_2 the $^{31}P\{^1H\}$ NMR spectrum of $[Pt(AuPPh_3)_8](NO_3)_2$ changed due to cluster decomposition. The rate data also showed that HD started forming after about 1 hour due to cluster fragmentation. The presence of both PPh_3 and H_2 therefore led to cluster fragmentation, while solutions of $[Pt(AuPPh_3)_8](NO_3)_2$ and PPh_3 without H_2 were stable for at least 12 h.

(34) The solubilities of H_2 and D_2 are very similar (generally within several percent) in nonaqueous solvents so this is a good approximation. See for example: Fogg, P. G. T.; Gerrard, W. *Solubility of Gases in Liquids*; John Wiley & Sons: Chichester, U.K., 1991. Cook, M. W.; Haxson, D. N.; Alder, B. J. *J. Chem. Phys.* **1957**, *26*, 748. Young, C. L. *Solubility Data Series, Hydrogen and Deuterium*; Pergamon Press: Oxford, U.K., 1981; Vol. 516. Hostetler, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 7629.

Table 3. Thermodynamic Results for the Reaction $[Pt(AuL)_8](NO_3)_2 + H_2 = [Pt(H)_2(AuL)_8](NO_3)_2$ in Solution[a]

solvent	L	T, °C	$[H_2]$ $(\times 10^4)^b$	$[MH_2]/[M]^c$	K (L mol^{-1})^d
nitrobenzene	PPh$_3$	30	4.9	0.82	1.7×10^3
nitrobenzene	PPh$_3$	6	3.4	1.09	3.2×10^3
nitrobenzene	P(p-tolyl)$_3$	6	3.4	5.26	1.5×10^4
acetonitrile	PPh$_3$	6	15	1.40	9.3×10^2
acetonitrile (2 mol equiv of PPh$_3$)^e	PPh$_3$	6	15	1.40	9.3×10^2
acetonitrile/nitrobenzene^f	PPh$_3$	6	8.6	1.20	1.4×10^3
acetonitrile/toluene^f	PPh$_3$	6	17	1.58	0.93×10^3

[a] See Experimental Section for details; 0.5 atm of H$_2$ was used in all of these measurements. [b] The [H$_2$] values at 0.5 atm partial pressure equal 0.5 times the measured [H$_2$] values at 1 atm. [c] Determined from ^{31}P NMR data. [d] The equilibrium constant $K = [Pt(H)_2(AuL)_8(NO_3)_2]/[Pt(AuL)_8(NO_3)_2][H_2]$ and has an estimated error of ±5%. [e] A 2 mol excess of PPh$_3$ ligand was added to the solution (see text). [f] Solvent mixtures were 1:1, v/v.

Table 4. Rate Data for HD Production for $M' = [Pt(H)(PPh_3)(AuPPh_3)_7](NO_3)_2$ and $M = [Pt(AuPPh_3)_8](NO_3)_2$ at Different Partial Pressures of $(H,D)_2{}^a$

$P_{(H,D)_2}$ (atm)^a	$[(H,D)_2]$ $(\times 10^4)^b$	turnover rate for M' ((mol of HD)/(mol of M'))(s)^c	turnover rate for M ((mol of HD)/(mol of M$_T$))(s)^d	$[M(H)_2]$ $(\times 10^4)^e$	turnover rate for MH$_2$ ((mol of HD)/(mol of MH$_2$))(s)^e
1.00	9.70	7.7	7.5	2.61	12.5
0.80	7.76	5.8	5.2	2.40	9.3
0.60	5.82	4.9	3.4	2.06	7.0
0.40	3.88	3.1	2.1	1.70	5.1
0.20	1.94	1.5	f		f

[a] Reactions run at 30 °C, 6.0 mL of NO$_2$Ph solution, total pressure = 760 Torr, P_{H_2} (partial pressure of H$_2$) from H$_2$, D$_2$, and Ar mixtures where volume of H$_2$ = volume of D$_2$. [b] From NMR measurement of H$_2$ solubilities (Experimental Section) and with use of Henry's law. [c] [M'] = 4.4×10^{-4} mol/L, mol in reactor = 2.6×10^{-6}. [d] M_T = [M] + [MH$_2$] = 4.2×10^{-4} mol/L, mol in reactor = 2.5×10^{-6}. [e] [MH$_2$] = [M(H,D)$_2$] and calculated from [H$_2$] = [(H,D)$_2$] and K for eq 1 (Table 3) with use of the relations [MH$_2$] = $RM_T/(1 + R)$ where $R = K[H_2]$ = [MH$_2$]/[M]. [f] Could not be determined due to experimental difficulties.
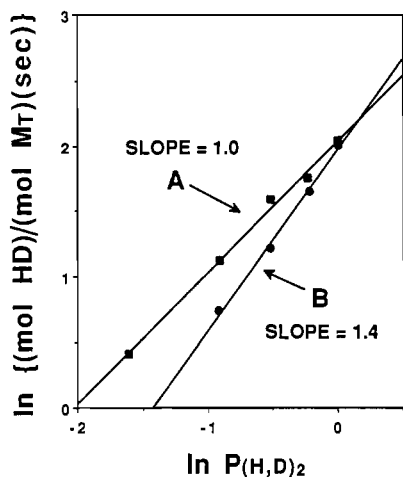

Figure 5. Rate dependence for HD production on the partial pressure of $(H,D)_2$ for nitrobenzene solutions of (A) $[Pt(H)(PPh_3)(AuPPh_3)_7]$-$(NO_3)_2$ and (B) $[Pt(AuPPh_3)_8](NO_3)_2$ from the data in Table 4. In this plot, the turnover rate is defined as (mol of HD)/(mol of M$_T$)(s), where mol of M$_T$ is the total moles of cluster in the reactor.

were found to irreversibly react with H$_2$ to give the stable 18-electron hydrido clusters $[Pt(H)(AgNO_3)(AuPPh_3)_8]NO_3$ and $[Pt(H)(CuCl)(AuPPh_3)_8](NO_3)$, respectively.[35] Note that the rates of HD production for $[Pt(AgNO_3)(AuPPh_3)_8](NO_3)_2$ and $[Pt(H)(AgNO_3)(AuPPh_3)_8]NO_3$ were very similar, suggesting that the latter compound was responsible for the catalysis. The only other clusters listed in Table 1 which had an observable reaction with H$_2$ were $[Pt(AuPPh_3)_8](NO_3)_2$ and its tri-p-tolylphosphine analog. In this case a fast and reversible reaction was observed (eq 1)^{1,2} with use of a variety of solvents (CH$_2$Cl$_2$, NO$_2$Ph, (CH$_3$)$_2$CO, CH$_3$CN). Although the other mixed metal–gold cluster compounds in this study did not show a detectable interaction with H$_2$, it is obvious that the clusters which catalyze H$_2$–D$_2$ equilibration must also interact. High-pressure (50 atm H$_2$) ^{31}P{^{1}H} NMR studies were carried out with $[Pt(AuPPh_3)_8]$-$(NO_3)_2$, $[Pt(H)(PPh_3)(AuPPh_3)_7](NO_3)_2$, and $[Pt(PPh_3)(Au-$

$PPh_3)_6](NO_3)_2$ in CD$_2$Cl$_2$ solution with use of a high pressure, sapphire NMR tube.[36] In the case of $[Pt(AuPPh_3)_8](NO_3)_2$, the position of equilibrium 1 shifted to the right showing complete conversion, while the other clusters showed no changes in their NMR spectra indicating that H$_2$ interaction was unobservable. There is indirect evidence, however, for the interaction of H$_2$ with $[Pt(PPh_3)(AuPPh_3)_6](NO_3)_2$ with use of pyridine as solvent. Pyridine is basic enough to deprotonate $[Pt(H)_2(AuPPh_3)_8]$-$(NO_3)_2$ to give the known[37] monohydrido cluster $[Pt(H)-$$(AuPPh_3)_8](NO_3)$ and HPy$^+$. This reaction was directly observed by ^{31}P{^{1}H} and ^{1}H NMR and was completely reversible. $[Pt-$$(AuPPh_3)_8](NO_3)_2$ quantitatively re-formed upon removal of H$_2$. Interestingly, $[Pt(PPh_3)(AuPPh_3)_6](NO_3)_2$ showed the same chemistry in pyridine solution. The known[37] monohydrido cluster $[Pt(H)(PPh_3)(AuPPh_3)_6](NO_3)$ reversibly formed under 1 atm of H$_2$ at 25 °C, providing evidence that H$_2$ does indeed react and become activated with $[Pt(PPh_3)(AuPPh_3)_6](NO_3)_2$. These reversible deprotonation reactions in pyridine solution will be the subject of a separate paper.[38]

**Thermodynamic and Kinetic Parameters from NMR Data for the Reaction of $[Pt(AuPPh_3)_8](NO_3)_2$ with H$_2$.** The equilibrium reaction between $[Pt(AuPPh_3)_8](NO_3)_2$ and H$_2$ (eq 1) has been observed by NMR and reported in a preliminary communication.[2] Between 40 and –60 °C, ^{31}P{^{1}H} and ^{1}H NMR spectra (Figures 6 and 7) of an equilibrium mixture of $[Pt(AuPPh_3)_8](NO_3)_2$ (M) and $[Pt(H)_2(AuPPh_3)_8](NO_3)_2$ (MH$_2$) under 0.5 and 1 atm H$_2$ partial pressures showed variable-temperature behavior characteristic of a two-site exchanging system with P–H, P–Pt, and H–Pt coupling. Resonances of the compounds M and MH$_2$ became frozen out at temperatures below ca. 25 °C in the ^{31}P{^{1}H} NMR, and in the ^{1}H NMR separate resonances of MH$_2$ and free H$_2$ were observed at ca. –20 °C. This behavior was qualitatively the same with nitrobenzene, acetonitrile, and dichloromethane solvents. The p-tolylphosphine derivative, {Pt[AuP(p-tolyl)$_3$]$_8$}-$(NO_3)_2$, showed a similar behavior with H$_2$ except that the reaction was more complete. In the slow-exchange regions, the clusters

(35) Private communication from Theo Kappen and Jan Steggerda, Univ. of Nijmegen, The Netherlands; manuscript in preparation.

(36) Roe, D. C. *J. Magn. Res.* **1985**, *63*, 388.
(37) Bour, J. J.; Schlebos, P. P. J.; Kanters, R. P. F.; Schoondergang, M. F. J.; Addens, H.; Overweg, A.; Steggerda, J. J. *Inorg. Chim. Acta* **1991**, *181*, 195.
(38) Aubart, M. A.; Koch, J. F. D.; Pignolet, L. H. *Inorg. Chem.*, in press.
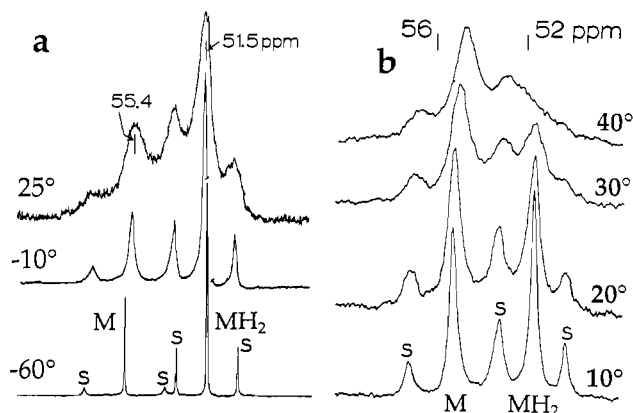
Figure 6. $^{31}P\{^1H\}$ NMR spectra of $[Pt(AuPPh_3)_8](NO_3)_2$ (3.6 × 10^{-3} M) at different temperatures with use of (a) CH_2Cl_2 as solvent at 1 atm H_2 pressure and (b) NO_2Ph as solvent at 0.5 atm H_2 pressure. The S symbols indicate ^{195}Pt satellites.
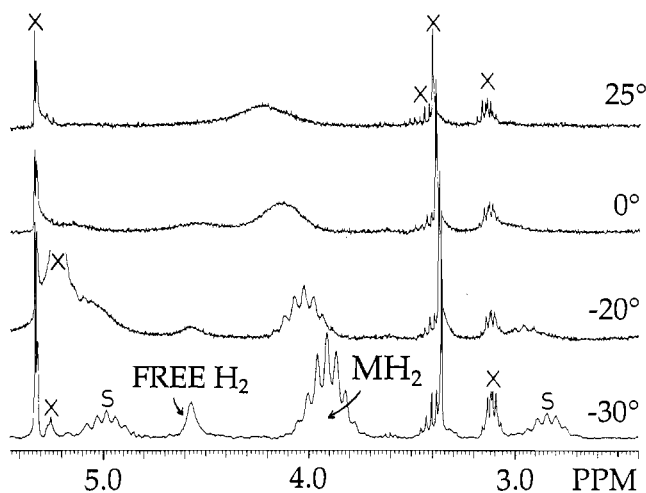
Figure 7. ^1H NMR spectra of $[Pt(AuPPh_3)_8](NO_3)_2$ (3.6 × 10^{-3} M) at different temperatures with use of CH_2Cl_2 as solvent at 1 atm H_2 pressure. The S symbols indicate ^{195}Pt satellites.

M and MH_2 are each nonrigid due to rapid skeletal rearrangements of the cluster cores. This process is well-known with clusters of this type and generally cannot be frozen out. NMR spectra of M and MH_2 are therefore simplified showing only single resonances with spin–spin coupling.

A comment is needed about the unusual, downfield chemical shift (δ ca. 3.9 ppm) of the hydrido ligands in $[Pt(H)_2(AuPPh_3)_8]$-$(NO_3)_2$, Figure 7. A number of Pt–Au cluster hydrides have been prepared and characterized.[2,8,37] All have ^1H NMR shifts downfield of TMS (e.g., $[Pt(H)(AuPPh_3)_8]^+$ (5.4 ppm), $[Pt(H)(PPh_3)(AuPPh_3)_7]^{2+}$ (2.3 ppm), and $[Pt(H)(PPh_3)(AuPPh_3)_6]^+$ (0.34 ppm)). The cause of these unusual shifts is unknown. T_1 values for the hydrido signals in $[Pt(H)_2(AuPPh_3)_8]^{2+}$ and $[Pt(H)(PPh_3)(AuPPh_3)_7]^{2+}$ have been determined and gave similar, long values (700 and 600 ms, respectively, at –30 °C)[2] providing strong evidence that the hydrido ligands in $[Pt(H)_2$-$(AuPPh_3)_8]^{2+}$ are classically bonded, probably bridging Pt–Au bonds.[2,8,37]

The equilibrium constants ($K = [MH_2]/[M][H_2]$) were determined for reaction 1 with use of nitrobenzene and acetonitrile as solvents at several temperatures from $^{31}P\{^1H\}$ NMR data and experimentally determined H_2 solubilities (see Experimental Section for details). The results are reported in Table 3. Values are also reported for the reaction in the presence of 2 equiv of added PPh_3 and for several solvent mixtures. These results will be discussed in the next section. Most of the values for K were determined at low temperature (6 °C) because the NMR spectra at higher temperatures were broadened due to exchange between M and MH_2 (Figure 6). More accurate values could therefore

be measured at the lower temperature. Rate data for the exchange between M and MH_2 were determined by a standard line shape analysis of the $^{31}P\{^1H\}$ NMR spectrum at 30 °C with use of the program DNMR5.[39] The kinetic analysis is completely described in the Experimental Section and gave values $\tau(M) = (2.7 \pm 0.1)$ × 10^{-3} s and $\tau(MH_2) = (2.2 \pm 0.1)$ × 10^{-3} s for the lifetimes of the exchanging species M and MH_2, respectively, for the following conditions: 30 °C, 0.5 atm H_2, total cluster concentration = 3.6 × 10^{-3} mol/L in nitrobenzene solution. It was sufficient to determine the rate data for reaction 1 at only one temperature for the purpose of evaluating the importance of this step in the catalytic HD equilibration reaction (see next section). Although a line shape analysis was not carried out with the ^1H NMR data (Figure 7), a qualitative estimate of the lifetimes near the coalescence temperature of ca. 5 °C gave results which were consistent with the ^{31}P NMR data.

Isotope Effects. In this study we have assumed that the effects of isotopes H and D on gas solubility, thermodynamics and kinetics of reaction 1, and the rate of catalytic H_2–D_2 equilibration are negligible. There is evidence in the literature that the solubilities of H_2 and D_2 in various solvents are very similar, generally within 2–3%.[34] Although this difference is important in studies which focus on isotope effects, it will not affect any of the results or conclusions in this paper. We measured the ratio $[MH_2]/[M]$ for reaction 1 with H_2 and D_2 separately by ^{31}P NMR (nitrobenzene solvent, 0.5 atm, 6 °C) and found that they were the same within experimental error. In addition, the values of k_{obs} for catalytic H_2–D_2 equilibration (nitrobenzene solvent, 1 atm, 30 °C) with initial gas mixtures of H_2:D_2 of 10:90 and 90:10 are the same within experimental error. These results confirmed the above assumptions.

Mechanism of the Homogeneous, Catalytic H_2–D_2 Equilibration Reaction. The evidence presented above shows that the H_2–D_2 equilibration carried out in solution phase is a true homogeneous reaction. In addition, mechanisms which lead to HD production do not involve heterolytic cleavage of H_2 because there is *no exchange with water, ethanol, or solvent* under the catalytic reaction conditions for any of the clusters studied. NMR and UV–vis spectroscopy showed that cluster fragmentation was not observed under catalytic reaction conditions. If cluster break-up into unobservable fragments was the cause of the H_2–D_2 equilibration catalysis, the fragments would have to be extremely active. We feel this is very unlikely. The fragments would have to exhibit turnover rates in excess of 50 s^{-1}. This is faster than rates measured for activated Pt surfaces.[22] The most likely fragments are small gold or Pt–Au phosphine clusters. Gold clusters are inactive for H_2–D_2 equilibration while the smaller Pt–Au clusters and monometallic Pt phosphine compounds are much less active than larger Pt–Au clusters (Table 1). If catalytically significant cluster fragments were formed, their high activity would make them very susceptible to poisoning by donor ligands such as PPh_3 or CO. Addition of 1 mol equiv of PPh_3 to an active $[Pt(AuPPh_3)_8](NO_3)_2$ catalyst system showed no inhibition (Table 2). The addition of 0.4 mol equiv of CO gave turnover rates only slightly lower, consistent with the formation of about 30% $[Pt(CO)(AuPPh_3)_8](NO_3)_2$ (Table 2) as expected. These results provided strong evidence that the H_2–D_2 equilibration was *not* caused by cluster fragmentation.

The catalysis reaction is therefore clean and results from H_2 and D_2 activation at the metal core of the cluster. There are two types of clusters that give good reaction rates, 16-electron clusters exemplified by $[Pt(AuPPh_3)_8](NO_3)_2$ and 18-electron hydrido clusters exemplified by $[Pt(H)(PPh_3)(AuPPh_3)_7](NO_3)_2$. Since the former type of cluster does not contain hydride ligands, the production of HD must involve the addition of *two* molecules of reactant (H_2 and D_2) to the same cluster. It is very unlikely that

(39) This computer program is available from the QCPE at Indiana University, QCMP 059.

pathways involving collisions between two clusters are important because the PPh₃ ligands completely shield the cluster cores, the reaction is first-order in cluster concentration, and molecular solids of the clusters are also excellent catalysts. With hydrido clusters, only one molecule of H_2 or D_2 is needed to produce HD. We have focused the mechanistic study on these two prototype clusters with the mechanistically more demanding 16-electron $[Pt(AuPPh_3)_8](NO_3)_2$ receiving the most attention.

Discussion of Mechanism for $[Pt(AuPPh_3)_8](NO_3)_2$. This cluster offered the best opportunity for a mechanistic study because the reversible addition of H_2 was directly observed by NMR. The results presented in the previous sections are consistent with a mechanism that involves the stepwise addition of two molecules of $(H,D)_2$ to the cluster M leading to a 20-electron, tetra(hydrido–deuterio) species $M(H,D)_4$. Such an intermediate or activated complex will rapidly scramble H and D and give HD *via* the reverse reactions. A similar mechanism has been proposed for catalytic H_2–D_2 equilibration by *trans*-Ir(X)(CO)(PPh₃)₂ (X = Cl, Br, I) and can be represented by eq 2 [24] In this equation, M

$$M \underset{-(H,D)_2}{\overset{+(H,D)_2}{\rightleftarrows}} M(H,D)_2 \underset{-(H,D)_2}{\overset{+(H,D)_2}{\rightleftarrows}} M(H,D)_4 \qquad (2)$$
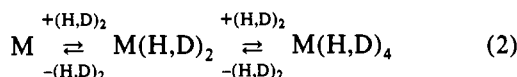
= $[Pt(AuPPh_3)_8](NO_3)_2$ and $(H,D)_2$ represents the three possibilities H_2, D_2, and HD. The integrated form of the rate law given in eq 3 was derived from this mechanism, where $[HD]_t$ and

$$t = \frac{1}{k_2[M(H,D)_2]} \ln\left(\frac{[HD]_e}{[HD]_e - [HD]_t}\right) \qquad (3)$$

$[HD]_e$ are the molar concentrations of HD in solution at time t and at equilibrium, respectively, $[M(H,D)_2]$ is the sum of the molar concentrations of $M(H)_2$, $M(D)_2$, and $M(HD)$, and *k_2 is the second-order rate constant for the formation of tetrahydrido species $(M(H,D)_2 + (H,D)_2 \overset{k_2}{\rightarrow} M(H,D)_4)$.* The complete derivation of eq 3 is given in ref 24. The following assumptions were made: (a) the term $[M(H,D)_2]$ in eq 3 remains constant during the equilibration reaction; (b) the solubilities of H_2, D_2, and HD are identical and equal to the solubility of H_2; (c) the equilibrium and rate constants for the reactions with H_2, D_2, and HD are identical. These assumptions are approximately valid for this system (vide infra).

Equation 3 fits the rate data as shown in Figure 3 for $[Pt(AuPPh_3)_8](NO_3)_2$ and for the other clusters studied. The slope of the line in Figure 3 defined as k_{obs} therefore equals $k_2[M(H,D)_2]$ in s⁻¹. It was shown from NMR line shape analysis results that the rate of step one in eq 2, the addition of the first H_2 to $[Pt(AuPPh_3)_8](NO_3)_2$, is more than 10³ times faster than the observed rate of HD production (see Experimental Section for this calculation). *The rate-determining step in eq 2 is therefore not the first step.* This indicates that the formation of a tetra(hydrido–deuterio) species such as $M(H,D)_4$ is the rate-limiting step. This is reasonable because the formation of a 20-electron M–Au cluster is expected to be difficult. Twenty-electron M–Au clusters have yet to be observed. The same conclusion was made for the catalytic H_2–D_2 equilibration by *trans*-Ir(X)(CO)(PPh₃)₂, where the data showed that the rate determining step was the formation of the tetrahydrido, Ir(V) intermediate or activated complex.[24] It follows from the above mechanism that the observed rate of HD production is given by eq 4. Equation 4 requires that the rate

rate of HD production = $k_2[M(H,D)_2][(H,D)_2]$ (4)

of HD production is first order in $[M(H,D)_2]$ and $[(H,D)_2]$. The kinetic data for variation of cluster concentration and partial pressure of $(H,D)_2$, $P_{(H,D)_2}$, are in complete agreement with this.

The rate dependence for HD production on $[Pt(AuPPh_3)_8](NO_3)_2$ concentration was first order as shown in Figure 4.[32] The
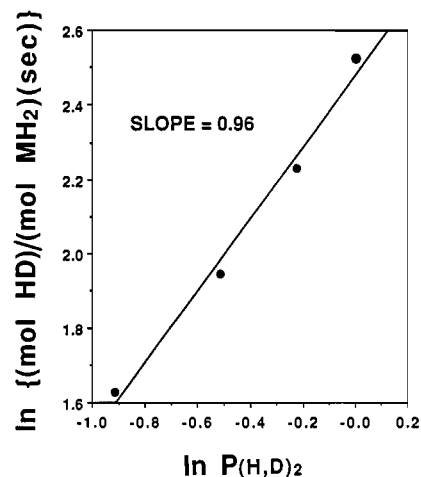
Figure 8. Replot of the data in Figure 5 for $[Pt(AuPPh_3)_8](NO_3)_2$ except that the turnover rate is now defined as (mol of HD)/(mol of MH_2)(s), i.e., turnovers per mole of the dihydride MH_2.

rate dependence for HD production on $P_{(H,D)_2}$ is shown in Figures 5 and 8. In Figure 5 the rate is defined as the usual turnover rate, (mol of HD)(s)⁻¹$(M_T)^{-1}$, where $M_T = [M(H,D)_2] + [M]$. This ln–ln plot shows first-order dependence on $P_{(H,D)_2}$ for the 18-electron hydrido cluster $[Pt(H)(PPh_3)(AuPPh_3)_7](NO_3)_2$ but greater than first-order dependence for the 16-electron cluster $[Pt(AuPPh_3)_8](NO_3)_2$. This is consistent with the proposed mechanisms for these two clusters (vide infra). In the case of $[Pt(AuPPh_3)_8](NO_3)_2$, eq 4 requires first-order dependence on $P_{(H,D)_2}$ but this can only be determined when $[M(H,D)_2]$ is held constant. Since an increase of $P_{(H,D)_2}$ also increases $[M(H,D)_2]$, the plot in Figure 5 is expected to show a slope greater than 1. A replot of the data in Figure 5 using the rate divided by $[M(H,D)_2]$ (or turnover rate for $M(H,D)_2$; see Table 4) is shown in Figure 8 and gives a slope of 0.96, in good agreement with eq 4. For the cluster $[Pt(H)(PPh_3)(AuPPh_3)_7](NO_3)_2$, where the addition of the second $(H,D)_2$ molecule is unnecessary for HD production (a hydride is already present in the starting cluster), the order with respect to $P_{(H,D)_2}$ was 1.0 (Figure 5). This result confirms the first-order dependence on $P_{(H,D)_2}$ for the rate-limiting steps with both clusters.

Although the mechanism shown by eq 2 for $[Pt(AuPPh_3)_8](NO_3)_2$ is reasonable and consistent with the above rate data, the observation of inhibition by the addition of more than 2 mol equiv of PPh₃ indicated that an additional step was required for HD production. The most reasonable explanation for this observation is that a PPh₃ ligand reversibly dissociates from the dihydride cluster $[Pt(H)_2(AuPPh_3)_8](NO_3)_2$ to give a reactive, coordinatively unsaturated species (eq 5). The addition of excess

$$[Pt(H)_2(AuPPh_3)_8](NO_3)_2 \rightleftarrows$$
$$[Pt(H)_2(Au)(AuPPh_3)_7](NO_3)_2 + PPh_3 \quad (5)$$
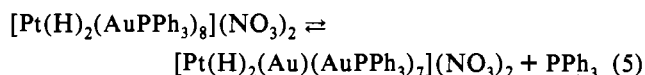
PPh₃ would shift equilibrium 5 to the left by Le Chatelier's Principle, thus decreasing the amount of the catalytically active species. This mechanism is appealing for several reasons: (1) it explains the increase in turnover rate for very dilute solutions of cluster (vide supra) because the fraction of dissociated species will increase with dilution; (2) it explains why $[Pt(H)_2(AuPPh_3)_8](NO_3)_2$ undergoes slow ligand exchange with added $P(p\text{-tolyl})_3$ (recall that $[Pt(AuPPh_3)_8](NO_3)_2$ does not); (3) it helps rationalize the formation of the 20-electron, tetrahydrido species from $[Pt(H)_2(AuPPh_3)_8](NO_3)_2$ by providing an open Au site to bind the incoming D_2. Formally, the loss of a PPh₃ ligand from Au does not decrease the electron count of the cluster core,[14–16] but large clusters of this type may significantly rearrange to become activated. This type of mechanistic step is also common in homogeneous catalysis with organometallic compounds.

At this point we favor the mechanism for catalytic HD production given by eq 6 where M* represents M less one PPh$_3$.

$$M \underset{-(H,D)_2}{\overset{+(H,D)_2}{\rightleftharpoons}} M(H,D)_2 \underset{+PPh_3}{\overset{-PPh_3}{\rightleftharpoons}} M^*(H,D)_2 \underset{-(H,D)_2}{\overset{+(H,D)_2}{\rightleftharpoons}} M^*(H,D)_4 \quad (6)$$
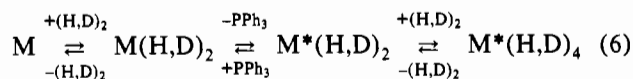
The rate law given by eq 3 is still consistent with this mechanism. A more complete study of the PPh$_3$ inhibition as a function of PPh$_3$ concentration would be useful, but such a quantitative study has proved difficult due to cluster decomposition in the presence of H$_2$ and PPh$_3$ (see ref 33). The observation of this PPh$_3$ dissociation step for cluster activation raises interesting questions about the nature of the tetrahydrido species and about the mechanism of the solid state reaction.

Discussion of Mechanism for [Pt(H)(PPh$_3$)(AuPPh$_3$)$_7$](NO$_3$)$_2$. The 18-electron, hydrido clusters are also good catalysts for H$_2$–D$_2$ equilibration in solution and do not cause H/D exchange with the solvent or added water or alcohol. The presence of a hydride or deuteride ligand in the starting cluster provides an easier mechanism for HD production. The rate data for [Pt(H)(PPh$_3$)-(AuPPh$_3$)$_7$](NO$_3$)$_2$ presented in Figure 5 and discussed above are consistent with a mechanism where the rate-limiting step is the addition of (H,D)$_2$ to give a 20-electron, M(H,D)$_3$ intermediate or activated complex. Such an intermediate would rapidly scramble H and D, and the reverse reaction would produce HD. In agreement with this, NMR results showed that [Pt(H)(PPh$_3$)-(AuPPh$_3$)$_7$](NO$_3$)$_2$ was rapidly converted into [Pt(D)(PPh$_3$)-(AuPPh$_3$)$_7$](NO$_3$)$_2$ under a D$_2$ atmosphere with nitrobenzene as solvent. PPh$_3$ inhibition experiments with [Pt(H)(PPh$_3$)-(AuPPh$_3$)$_7$](NO$_3$)$_2$ showed similar results to those observed with [Pt(AuPPh$_3$)$_8$](NO$_3$)$_2$. Therefore a reversible and spectroscopically unobservable dissociation of PPh$_3$ is implicated for activation, just as with [Pt(AuPPh$_3$)$_8$](NO$_3$)$_2$.

General Comments on Mechanism. The above results for [Pt-(AuPPh$_3$)$_8$](NO$_3$)$_2$ in solution are in agreement with the mechanism shown by eq 6. The fact that this cluster catalyzes H$_2$–D$_2$ equilibration in the solid state at faster rates than in solution is surprising, especially since a phosphine dissociation step is implicated in solution. Crystals of these clusters are very porous and contain a significant amount of empty space due to the loss of solvent upon removal from the crystallizing solution. Single-crystal X-ray analysis of these compounds requires special crystal handling techniques such as sealed capillary tubes that contain some solvent. Even with this technique the solvent molecules, counteranions, and sometimes the ligand phenyl rings are disordered. It is possible that a PPh$_3$ ligand can partially dissociate in the solid, especially after solvent loss, thus producing an activated cluster. We have recorded a ^{31}P MAS solid-state NMR spectrum of microcrystalline [Pt(AuPPh$_3$)$_8$](NO$_3$)$_2$. There is no evidence of free PPh$_3$, and the chemical shift of the cluster is similar to that in solution. The spectrum has not been recorded in the solid state under a H$_2$ atmosphere however. More work is needed to understand this heterogeneous, catalytic reaction. Current studies are aimed at measuring the effect of the ligand, counteranion, and crystallizing solvent.

Finally, one would expect the 18-electron, non-hydrido, Pt–Au clusters to be inactive for H$_2$–D$_2$ equilibration. Indeed, they show activity about 10 times lower than the 16-electron clusters. Their small activity probably resulted from dissociation of the ligand bound to Pt. For example, the activity of [Pt(CO)-(AuPPh$_3$)$_8$](NO$_3$)$_2$ increases slightly with repeated runs but decreases to zero after purging the reaction mixture with CO followed by the usual degassing. On the other hand, the very stable, 18-electron supracluster, Pt$_2$(AuPPh$_3$)$_{10}$Ag$_{13}$Cl$_7$, is inactive for H$_2$–D$_2$ equilibration, confirming the notion that 18-electron clusters are not catalysts for this reaction.

It is interesting to speculate on the nature of the 20-electron intermediates or transition states M(H,D)$_4$ and M(H,D)$_3$. We

have been unable to directly observe these species even by high-pressure NMR experiments to 80 atm of H$_2$. A number of mixed metal–gold hydrido clusters are now known, and in all cases the hydrides are either known or thought to be bridging (doubly or triply) between the transition metal and gold atoms.[40] It is likely that the 20-electron species also contain bridging hydrido ligands, but the possibility of a side-bonded η^2-H$_2$ cannot be ruled out. In order to test the possibility that the second (H,D)$_2$ adds in this fashion, we carried out H$_2$–D$_2$ equilibration experiments with 1:1 (H$_2$ + D$_2$)–N$_2$ and (H$_2$ + D$_2$)–Ar mixtures with [Pt(AuPPh$_3$)$_8$]-(NO$_3$)$_2$ and nitrobenzene as solvent. N$_2$ is known to compete with η^2-H$_2$ binding in many monometallic organometallic compounds.[41] The results showed that the rate of HD production for these two experiments was the same within experimental error.

Conclusions. Mixed Pt–Au cluster compounds have been shown to be excellent and clean catalysts for H$_2$–D$_2$ equilibration under homogeneous and heterogeneous conditions. These compounds therefore have the potential to serve as *models* for bimetallic surface catalysts. There is a significant rate effect on metal composition. The most important effects are (a) faster rates were observed as the Au/Pt ratio increased, (b) Pt-centered clusters gave faster rates than Pd-centered clusters and Au clusters were inactive, and (c) 16-electron clusters gave much faster rates than 18-electron clusters, but eighteen-electron hydrido clusters were also fast. These trends suggest that M–Au bonds may function as active sites for H$_2$ activation (M–Au cluster hydrides have bridging μ-H bonding modes) with Pt–Au bonds being more effective than Pd–Au bonds. This result helps explain how Au can increase the activity of Pt–Au surfaces and suggests that Au may play a direct role in H$_2$ activation. These suggestions are complicated, however, by the fact that PPh$_3$ dissociation is necessary for catalyst activation. The open Au site may be necessary for binding (H,D)$_2$ so that H/D exchange can take place on the cluster. Weak binding of substrates by Au in Pt–Au surface catalysts has been observed.[4b]

The mechanism for catalytic H$_2$–D$_2$ equilibration under homogeneous conditions has been extensively studied for the 16-electron cluster [Pt(AuPPh$_3$)$_8$](NO$_3$)$_2$ by a combination of kinetic and spectroscopic experiments. The results support a three-step mechanism shown by eq 6 in which the addition of the first (H,D)$_2$ molecule and the PPh$_3$ dissociation steps are fast. The rate-limiting step is the addition of a second (H,D)$_2$ molecule giving a 20-electron, tetrahydrido intermediate or activated complex. The creation of an open Au site is implicated to be important for H$_2$–D$_2$ equilibration. The mechanism with the hydrido, 18-electron cluster [Pt(H)(PPh$_3$)(AuPPh$_3$)$_7$](NO$_3$)$_2$ is thought to involve the addition of only one molecule of (H,D)$_2$ giving a 20-electron, trihydrido activated complex. The 20-electron species have not been directly observed.

Experimental Section

General Procedures. ^{31}P{^{1}H} and ^{1}H NMR spectra were recorded at 121.4 and 300 MHz, respectively, with use of a Varian VXR-300 MHz spectrometer. ^{31}P{^{1}H} NMR spectra were run with proton decoupling and shifts are reported in ppm relative to internal standard trimethyl phosphate (TMP) with positive shifts down field. Solvents were dried, distilled, and stored under nitrogen prior to use, although the addition of small amounts of water did not significantly affect the kinetic or thermodynamic results. H$_2$ and D$_2$ were obtained from Matheson and used without further purification. N$_2$ and Ar were purified with use of a BASF catalyst column. Gas transfers were carried out with use of gastight syringes, and the amounts were determined either volumetrically or by pressure measurement. Gas mixtures were prepared volumetrically.

(40) (a) Alexander, B. D.; Johnson, B. J.; Johnson, S. M.; Casalnouvo, A. L.; Pignolet, L. H. *J. Am. Chem. Soc.* **1986**, *108*, 4409. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F.; Albinati, A. *Inorg. Chem.* **1992**, *31*, 3841. (c) Mueting, A. M.; Bos, W.; Alexander, B. D.; Boyle, P. D.; Casalnuovo, J. A.; Balaban, S.; Ito, L. N.; Johnson, S. M.; Pignolet, L. H. *New J. Chem.* **1988**, *12*, 505.
(41) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95.

All of the cluster compounds used in the kinetic studies were synthesized as described in the literature (references are given in Table 1) except for the new cluster {Pt[AuP(p-tolyl)₃]₈}(NO₃)₂ (see below). Purity was checked by ^{31}P{^{1}H} NMR, and all of the compounds were at least 98% pure by this method. Compound syntheses and sample preparations were carried out under a purified N₂ or Ar atmosphere with use of standard Schlenk or glovebox techniques.

Synthesis of {Pt[AuP(p-tolyl)₃]₈}(NO₃)₂. This compound was prepared with a similar procedure to that of its PPh₃ analogue except there are several important differences.[42] The starting materials Au(P)NO₃ and Pt(P)₃, where P = P(p-tolyl)₃, were prepared by following standard literature procedures for the PPh₃ analogues.[43,44] Solid Pt(P)₃ (54 mg, 0.049 mmol) was dissolved in 50 mL of freshly distilled THF under a continuous H₂ purge, and the mixture was stirred at room temperature for 10 min. Solid Au(P)NO₃ (214 mg, 0.38 mmol) was slowly added to the stirred solution under a H₂ purge. The solution darkened and was stirred for ca. 12 h. The solvent was pumped off and the dry residue redissolved in ca. 8 mL of MeOH and crystallized by the slow addtion of ca. 70 mL of (Et)₂O. Dark red crystals (80 mg) formed after standing for several days. The red-brown crystals were isolated and washed with 2 × 5 mL portions of (Et)₂O. The yield was 38%. Characterization by ^{31}P NMR and FABMS confirmed that the title cluster had been made. ^{31}P NMR (CD₃OD, 20 °C): δ 53.2, J_{Pt-P} = 495 Hz. FABMS (m/e) (see ref 15 for experimental details): major peaks of mass 4267.3 obs, 4267.7 calcd for (Pt(AuP)₈(NO₃) = M)⁺; 4205.3 obs, 4205.7 calcd for (M – (NO₃))⁺; 3963.0 obs, 3963.3 calcd for (M – (P))⁺; 3901.1 obs, 3901.3 calcd for (M – (NO₃) – (P))⁺; 3658.6 obs, 3659.0 calcd for (M – 2(P))⁺; 3596.8 obs, 3597.0 calcd for (M – (NO₃) – 2(P))⁺.

NMR Sample Preparation. NMR samples used for the determination of thermodynamic and kinetic (line shape analysis) parameters for the reaction shown in eq 1 were prepared by transferring 0.700 mL of a solution of known concentration of cluster compound into an NMR tube equipped with a rotationally symmetrical valve obtained from J. Young Scientific Glassware (distributed by the Brunfeldt Co., Bartlesville, OK). The valve is equipped with an extended Teflon piston with an O-ring seal and was connected via a gas adapter and stopcock to a vacuum line by rubber tubing. The solution was freeze–pump–thawed and warmed to room temperature while sealed under vacuum. The gas was then added to the head space above the solution to give a total pressure of 760 Torr + the solvent (or solvent mixture) vapor pressure at that temperature. This procedure was repeated three times. Solvent vapor pressures were determined by allowing the system to come to equilibrium without the addition of gas. The total pressure of the head space was determined with use of a manometer to ±1 Torr. H₂ partial pressures of less than 760 Torr were achieved with use of H₂/Ar mixtures. The NMR tube was then sealed with the J. Young valve, disconnected from the vacuum line, and placed into the spectrometer at the appropriate temperature. The sample tube was twice removed from the spectrometer, quickly shaken, and replaced to speed up the gas–solution equilibration. Equilibration was achieved in about 1 h as determined by repeated NMR integrations as a function of time. The sample shaking procedure was absolutely necessary to achieve equilibrium.

Thermodynamic and Kinetic Modeling of Reaction 1. Between 40 and –60 °C, ^{31}P{^{1}H} and ^{1}H NMR spectra (Figures 6 and 7) of an equilibrium mixture of [Pt(AuPPh₃)₈](NO₃)₂ (M) and [Pt(H)₂(AuPPh₃)₈](NO₃)₂ (MH₂) under 380 and 760 Torr H₂ partial pressure show variable-temperature behavior characteristic of a two-site exchanging system. Equilibrium constants for reaction 1 (K = [MH₂]/[M][H₂]) in several solvents at 6 °C were determined from the ^{31}P{^{1}H} NMR spectra with use of the curve-fitting program from the Varian software and the experimentally determined concentration of dissolved H₂. Values from different determinations agreed within ±5% and are reported in Table 3. The concentration of dissolved H₂ in the solvents and solvent mixtures was determined experimentally at 760 Torr H₂ partial pressue. This was carried out by comparison of the integrated area of the ^{1}H NMR signal of dissolved H₂ at ca. 4.5 ppm to that of added 1,2-dichloroethane of known concentration. The concentration of 1,2-dichloroethane was adjusted to give signals of similar area. The concentration of H₂ for lower partial pressures from H₂/Ar mixtures was calculated with use of

Henry's law which states that the solubility is proportional to the partial pressure.[45] The [H₂] values measured at 760 Torr H₂ partial pressure wereas follows: nitrobenzene (30 °C) 9.7 × 10⁻⁴ mol/L, (6 °C) 6.8 × 10⁻⁴; acetonitrile, (30 °C) 3.8 × 10⁻³, (6 °C) 2.9 × 10⁻³; acetonitrile: nitrobenzene (1:1 v/v, 30 °C) 2.3 × 10⁻³, (6 °C) 1.7 × 10⁻³; acetonitrile: toluene, (1:1 v/v, 30 °C) 4.7 × 10⁻³, (6 °C) 3.4 × 10⁻³; acetonitrile: mesitylene (1:1 v/v, 30 °C) 4.1 × 10⁻³, (6 °C) 3.0 × 10⁻³. Note that the literature value for nitrobenzene at 25 °C and 760 Torr is 1.5 × 10⁻³ mol/L,[34] which is a little larger than the value determined by NMR. Literature values could not be found for acetonitrile or for the solvent mixtures.

Rate constants for the exchange between M and MH₂ in nitrobenzene solution were determined by a standard line shape analysis of the ^{31}P{^{1}H} NMR spectrum near coalescence at 30 °C with use of the program DNMR5.[39] Chemical shift, coupling constant, and line width parameters in the absence of exchange at this temperature were determined from frozen out spectra at lower temperatures in dichloromethane and nitrobenzene solutions (see Figure 6). The relative populations of the exchanging species M and MH₂ were determined from the experimental equilibrium constant data. The actual parameters used and the experimental and calculated spectra are given as supplementary material. It can be shown that, for the equilibrium reaction given by eq 7, the

$$M + H_2 \underset{k_{-1}}{\overset{k_2'}{\rightleftharpoons}} MH_2 \tag{7}$$
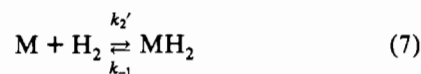
lifetime of species MH₂, $\tau(MH_2)$, = $1/k_{-1}$ where k_{-1} is the first-order rate constant for dissociation of MH₂, and the lifetime of species M, $\tau(M)$, = $\tau(MH_2)/R$, where R = [MH₂]/[M]. The second-order rate constant, k_2', can be calculated from the relations $\tau(M) = 1/(k_2'[H_2])$ and $K = k_2'/k_{-1}$ = [MH₂]/[M][H₂].[46] This line shape analysis (supplementary material) gave values of (2.7 ± 0.1) × 10⁻³ s and (2.2 ± 0.1) × 10⁻³ s for $\tau(M)$ and $\tau(MH_2)$, respectively, for the following conditions: 30 °C, 380 Torr H₂, [H₂] = 4.9 × 10⁻⁴ mol/L, [M_T] = 3.6 × 10⁻³ mol/L, R = 0.82, and K = 1.7 × 10³ L mol⁻¹ in nitrobenzene solution.

Rate Determinations for Catalytic H₂–D₂ Equilibration. The reactor consisted of a 30-mL, jacketed glass vessel equipped with a star-shaped, Teflon stir bar, a gas inlet tube connected to a vacuum line and manometer with stopcocks placed near the reactor, and a rubber septum for gas sampling. The temperature of the reactor was held at 30 ± 0.2 °C by circulating water from a temperature-controlled bath through the jacket which covered the entire reactor. For catalysis reactions run under homogeneous conditions, a solution of cluster compound of known concentration was prepared with use of a 10-mL volumetric flask. Nitrobenzene solvent was used for all experiments where the rates of different clusters are compared, but acetonitrile and several solvent mixtures were also used for the mechanistic studies with [Pt(AuPPh₃)₈]-(NO₃)₂. The low vapor pressure of nitrobenzene, as well as its use as an internal control for heterogeneous impurities (vide infra), made it an excellent solvent for these catalytic studies. For each kinetic run, 6.0 mL of the cluster solution was transferred by pipet into the reactor and degassed by slow pumping for 5 min. Solvent loss due to the pumping was small and reproducible. The solution was rapidly stirred to produce a froth during the entire kinetic determination. The reaction rate did not depend on stirring rate, although stirring speed was not accurately controlled. Reaction conditions were selected so that gas–liquid diffusion was not rate limiting (vide infra). The initial gas mixture, which consisted of equal amounts of H₂ and D₂ (sometimes diluted with Ar or N₂), was injected into the evacuated reactor by gastight syringe to give a total pressure of 760 Torr + the vapor pressure of the solvent. For nitrobenzene, the solvent vapor pressure is less than 1 Torr at 30 °C. In a typical experiment the reactor was charged with ca. 3 × 10⁻⁶ mol of cluster and 1.31 × 10⁻³ mol of H₂ + D₂. The time of the injection was defined as time zero for the equilibration reaction. For catalysis reactions run under heterogeneous conditions (gas–solid reactions), the same reactor and

(42) Bour, J. J.; Kanters, R. P. F.; Schlebos, P. P. J.; Steggerda, J. J. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 211.

(43) Mueting, A. M.; Alexander, B. D.; Boyle, P. D.; Casalnuovo, A. L.; Ito, L. N.; Johnson, B. J.; Pignolet, L. H. *Inorganic Synthesis*; John Wiley & Sons: New York, 1992; Vol. 29, p 279.

(44) Jolly, W. L. *Inorganic Synthesis*; McGraw-Hill Book Co.: New York, 1968; Vol. XI, p 105.

(45) We have experienced difficulty in measuring the solubilty of H₂ with H₂/Ar and H₂/N₂ gas mixtures by the NMR method. Our data show deviations from Henry's law which are inconsistent with other measurements in this study. We suspect that this is due to some artifact of the NMR method where thermal gradients and poor gas mixing could cause difficulties.

(46) Hauger, B. E.; Gusev, D.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 208. See also: Oki, M. In *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH Publishers: Deerfield Beach, FL, 1985; Chapter 1.

conditions were used except that the solution was replaced with a solid sample of the cluster suspended in a glass bucket. Solid samples were either crystalline or finely powdered. The finest powdered solids were prepared by rapidly adding a solvent such as diethyl ether to a dichloromethane solution of the cluster to cause fast precipitation of the solid. Excessive grinding and direct stirring of the solid samples were avoided to prevent decomposition or heating.

Kinetic parameters were determined by measuring the mole percents of H_2, D_2, and HD in the gas head space as a function of time (see Figure 2). Gas samples of ca. 0.1 mL were taken by gastight syringe frequently during the course of the equilibration and injected into the inlet of a mass spectrometer tuned and calibrated in the mass 1–10 range. The mass spectrometer used was a Leybold Inficon Quadrex 200 residual gas analyzer. It was calibrated with gas mixtures of known composition and in contact with the same solvent system during each kinetic run. In addition, some runs were checked by gas chromatography as described by Yasumori,[47] and the same rate data was obtained. Rate constants for HD production (k_{obs}) were determined by plotting the equation $\ln\{[HD]_e/([HD]_e-[HD]_t)\} = k_{obs}t$ (see Figure 3), where $[HD]_e$ and $[HD]_t$ are the mole fractions of HD at equilibrium and at time t, respectively. $[HD]_e$ was calculated from the initial H_2 and D_2 concentrations and with use of $K_{eq} = 3.28$ at 30 °C for the reaction $H_2 + D_2 = 2HD$.[22,48] These plots were linear for all of the clusters studied in agreement with other H_2–D_2 equilibration catalysts.[24–27] The rate of HD production in (mol of HD)·(s)$^{-1}$ is defined as k_{obs}[mol of ($H_2 + D_2$ + HD)] where mol of ($H_2 + D_2$ + HD) = 1.31×10^{-3} for all experiments with 760 Torr partial pressure of ($H_2 + D_2$ + HD). The turnover rate is defined as the rate of HD production divided by the moles of cluster in the reactor and has the units

(mol of HD produced)(mol of cluster)$^{-1}$(s)$^{-1}$. Reactions were typically monitored for 1–2 h or until about 70% equilibrated. The turnover rates reported are precise to ± 5% as determined by repeating runs numerous times. The largest source of error seemed to be the presence of O_2 as a reactant impurity and from occasional leaks in the septa while transferring gases by syringe.

Comparison of the Rate of Reaction 1 to the Rate of HD Production. In order to evaluate which step in the proposed reaction mechanism (eq 2) is rate limiting for the catalyst $[Pt(AuPPh_3)_8](NO_3)_2$ (M), it is necessary to compare the observed rate of HD production to the rate of the first step (eq 1) in the mechanism. We have measured the rate of this first step by NMR line shape analysis (see above). If we assume that this reaction is rate limiting, it is straightforward to calculate the rate of HD production expected for a typical H_2–D_2 equilibration reaction (30 °C, 1 atm $(H,D)_2$, $[M_T] = 6.4 \times 10^{-4}$ mol/L, 6.0 mL nitrobenzene solution, Figures 2 and 3). The rate equals $(1/\tau(MH_2))$(mol of MH_2 in reactor) or $(4.5 \times 10^2 \text{ s}^{-1})(1.7 \times 10^{-6} \text{ mol}) = 7.7 \times 10^{-4}$ mol of HD/s. The observed rate of HD production is ca. 3×10^{-7} mol of HD/s. Since the rate of the first step is more than 10^3 times faster, this step is *not* rate limiting. The difference in rate is so large that this conclusion is valid even with the small differences between the NMR and catalysis experiments.

Supplementary Material Available: Text giving details of the line shape analysis and a figure showing the experimental and simulated ^{31}P NMR spectra (3 pages). Ordering information is given on any current masthead page.

(47) Yasumori, I.; Ohno, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1302.
(48) Steggerda, J. J.; Bour, J. J.; van der Velden, J. W. A. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 164.
(49) Cook, C. D.; Jauhal, G. S. *J. Am. Chem. Soc.* **1968**, *90*, 1464.
(50) Kanters, R. P. F.; Schlebos, P. P. J.; Bour, J. J.; Wijnhoven, J.; van den Berg, E.; Steggerda, J. J. *J. Organomet. Chem.* **1990**, *388*, 233.
(51) Schoondergang, M. F. J. Ph.D. Thesis, University of Nijmegen, The Netherlands, 1992.
(52) Bour, J. J.; Kanters, R. P. F.; Schlebos, P. P. J.; Bos, W.; Bosman, W. P.; Behm, H.; Beurskens, P. T.; Steggerda, J. J. *J. Organomet. Chem.* **1987**, *405*, 329.