Cluster Chemistry on Surfaces: Characterization and Catalytic Studies of Phosphine-Stabilized Platinum−Gold Clusters on Silica and Alumina Supports

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Received April 6, 1995[⊗]

Cationic, phosphine-ligated Pt−Au cluster compounds, $[Pt(AuPPh_3)_8](NO_3)_2$ (**1**) and $[(PPh_3)Pt(AuPPh_3)_6](NO_3)_2$ (**2**), have been immobilized on silica and alumina supports. Characterization of the supported clusters by ^{31}P MAS NMR, IR, and UV−visible spectroscopy and study by chemisorption and temperature-programmed desorption of CO show that the clusters are immobilized intact without measurable fragmentation or irreversible transformation. This is confirmed by quantitative desorption of the clusters. The reactivity of the supported clusters with CO and H_2 was found to be similar to the known reactivities in solution and molecular solid phases. The cluster $[(PPh_3)Pt(H)(AuPPh_3)_7](NO_3)_2$ (**3**) was also immobilized on silica and found to be intact by MAS ^{31}P NMR and desorption experiments. The turnover rate (TOR) for H_2-D_2 equilibration was determined for these supported clusters at room temperature. The clusters **1** and **2** were good catalysts on silica and alumina supports after treatment at 135 °C under vacuum (TOR = 10−20 s^{-1}), but showed significant activation by treatment at 110 °C under H_2 (TOR = 85−220 s^{-1}). Cluster **3**/SiO_2 gave a similar rate (TOR = 170 s^{-1}) with no thermal activation. All samples subjected to the thermolysis conditions given above were found to be intact by ^{31}P MAS NMR and could be quantitatively desorbed. The high activities of the supported Pt−Au clusters are believed to result from support-promoted, partial PPh_3 dissociation. Desorption experiments show that this dissociation is reversible.

Introduction

Supported molecular metal complexes and organometallic compounds have been extensively studied as novel catalysts and metal particle catalyst precursors.[1] For such systems it is of interest to determine the effect of the support on structure and reactivity of the metal complex. The field of surface organometallic chemistry deals with this topic and has recently received significant attention.[1−4] Studies in this field have primarily used transition metal carbonyl cluster compounds deposited on a variety of metal oxide supports.[1] This area of research is important because oxide-supported metals and some metallic complexes (especially of the bimetallic variety) catalyze many significant reactions.[1−8] Although supported molecular compounds are not likely to be practical catalysts themselves due to their instability, the study of their surface chemistry can provide useful insight into cluster reactivity and the mechanism of thermal activation. A long-range goal of our research in this area is to evaluate the use of cationic, phosphine-ligated Pt−Au cluster compounds as precursors to uniform, highly dispersed, supported Pt−Au particle catalysts. There has been significant interest in Pt−Au catalysts but in no case has a preformed bimetallic cluster been used in catalyst preparation.[7] In this paper we describe the preparation, characterization, and reactivity of the Pt−Au cluster compounds, $[Pt(AuPPh_3)_8](NO_3)_2$ (**1**), $[(PPh_3)Pt(AuPPh_3)_6](NO_3)_2$ (**2**), and $[(PPh_3)Pt(H)(AuPPh_3)_7](NO_3)_2$ (**3**), immobilized on silica and alumina supports. There have been very few studies of this type with cationic, phosphine-

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[⊗] Abstract published in *Advance ACS Abstracts*, January 1, 1996.

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ligated compounds,[2] and we are unaware of any with this class of cluster compounds.

These clusters are very well characterized in solid (single-crystal X-ray diffraction) and solution (NMR, IR, UV−visible spectroscopy) phases.[9−17] The solid-state structures of the metal cores of **1**−**3** are shown in Figure 1. The reaction chemistry of 16-electron clusters **1** and **2** with H_2 and CO has been thoroughly investigated.[13,15,18] Both react with one molecule of CO (1 atm) quantitatively in solution and solid phases to give the 18-electron adducts $[(CO)Pt(AuPPh_3)_8](NO_3)_2$ (**1(CO)**) and $[(PPh_3)(CO)Pt(AuPPh_3)_6](NO_3)_2$ (**2(CO)**), respectively. Cluster **1** reversibly adds one molecule of H_2 (1 atm) in solution and solid phases to give the dihydride $[Pt(H)_2(AuPPh_3)_8](NO_3)_2$ (**1(H)₂**).[15] The hydride ligands in **1(H)₂** are believed to be bridging between Pt and Au atoms. The 18-electron cluster **3** is unreactive with H_2 and slowly decomposes under a CO atmosphere.[19] All are good catalysts for H_2−D_2 equilibration in homogeneous (solution) and heterogeneous (molecular solid) phases.[14−17] The turnover rates (TOR's) for HD production (30 °C, 1 atm) for **1**, **2**, and **3** in nitrobenzene solution are 4.5, 1.3, and 4.6 min^{-1}, respectively.[16] The mechanism for the homogeneous, catalytic H_2−D_2 equilibration was studied by spectroscopic and kinetic measurements.[16,19] For cluster **1**, the mechanism involves the following steps:

$$\mathbf{1} + H_2 \rightleftharpoons \mathbf{1(H)_2} \tag{1}$$

$$\mathbf{1(H)_2} \rightleftharpoons \mathbf{1(H)_2{}^*} + PPh_3 \tag{2}$$

$$\mathbf{1(H)_2{}^*} + D_2 \rightleftharpoons \mathbf{1(H)_2(D)_2{}^*} \tag{3}$$

where an asterisk indicates a cluster with one less PPh_3 ligand. Step 1 was directly observed by NMR spectroscopy for **1**,[15,16] while steps 2 and 3 were implicated by rate measurements as a function of $[H_2]$, $[D_2]$, [cluster], and added $[PPh_3]$.[16,19] Step 3, the formation of a tetra(hydrido,deuterido) species and its reverse species lead to HD production. Cluster **2** is believed to have the same mechanism.[16,19] The mechanism with the monohydrido cluster **3** also involves PPh_3 dissociation followed by the addition of D_2 to give a tri(hydrido,deuterido) species or activated complex.[19] The PPh_3 dissociation step is plausible as it produces a cluster with a bare Au atom that can bind an incoming D_2 substrate (step 3) without the formation of a 20-electron intermediate. The rate of heterogeneous H_2−D_2 equilibration with microcrystalline samples of **1**−**3** was faster than that in homogeneous solution (TOR = 2−5 s^{-1}, 1 atm, 30 °C), but had a marked dependence on surface area.[16] The fast catalysis by molecular solid clusters intrigued us and provided the initial motivation to investigate the chemistry of these clusters immobilized on surfaces, where rate effects from gas diffusion can be better controlled. It was also of interest to determine the effect of rigid supports on cluster structure and reactivity. The fact that these clusters are very well characterized, are air and moisture stable, and carry out simple catalytic probe reactions (H_2−D_2 equilibration and ethylene hydrogenation) makes them excellent candidates for this study.

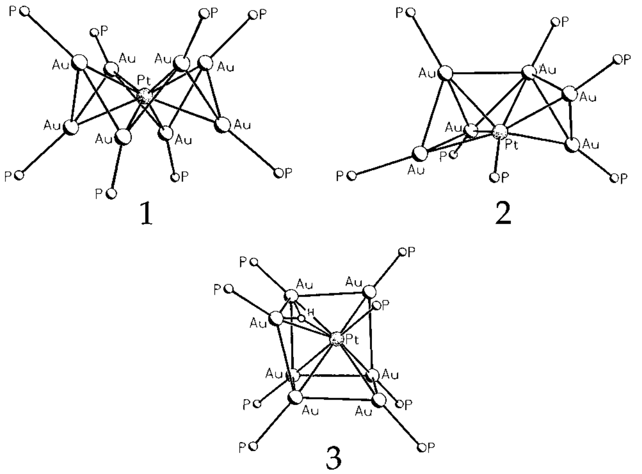

Figure 1. Solid state structures of the $Pt(AuP)_x$ cores of the clusters $[Pt(AuPPh_3)_8](NO_3)_2$ (**1**), $[(PPh_3)Pt(AuPPh_3)_6](NO_3)_2$ (**2**), and $[(PPh_3)Pt(H)(AuPPh_3)_7](NO_3)_2$ (**3**). The position of the hydride ligand in **3** was inferred from spectroscopic data, distortions in the metal core, and potential energy calculations (ref 12).

Results and Discussion

Preparation and Characterization. Clusters **1**−**3** were quantitatively adsorbed on silica and alumina (see Experimental Section for information on supports and support pretreatment) by the slow addition of a dilute CH_2Cl_2 solution of the cluster to a suspension of the support in CH_2Cl_2 with constant swirling. The yellow-colored solvent became clear within several minutes and was decanted off. The adsorption was found to be quantitative by UV−visible spectroscopy of the decanted solution, and typical cluster loadings are 1% by mass (0.05% Pt), although loadings as high as 10% were used in solid-state NMR experiments. The resulting yellow solid was dried under vacuum at room temperature (RT) for 1 h, except for some of the solid-state NMR experiments where air drying for 10 min was used. All samples of **1** and **2** supported on SiO_2 and Al_2O_3 for chemisorption and rate studies were then heated at 135 °C in a quartz reactor under high vacuum until pressures of ca. 5×10^{-8} Torr were achieved (1.5−2 h). Samples of **3**/SiO_2 were evacuated at RT until the same pressure was achieved (3−4 h). Heating samples of **3**/SiO_2 resulted in irreversible cluster decomposition so heating above RT was avoided (see below). The clusters, treated as described above, could be desorbed from alumina by washing with CH_3OH solvent. Complete desorption from silica required washing with CH_3OH saturated with KPF_6, suggesting that ion pairing is important. The desorption of the cationic clusters was *quantitative* as determined by UV−visible spectroscopy. In addition, high-resolution ^{31}P NMR of the desorbed species showed only the presence of the original cluster cations, indicating that *no measurable fragmentation or irreversible transformation of the immobilized clusters occurred.*

The supported clusters were investigated by ^{31}P MAS NMR, IR, and UV−visible spectroscopy, chemisorption of CO and H_2, temperature-programmed desorption (TPD) of CO, and kinetic measurements of H_2−D_2 equilibration. The rate of ethylene hydrogenation was also determined for **1** supported on SiO_2 and Al_2O_3. The ^{31}P MAS NMR (40.53 MHz) spectra

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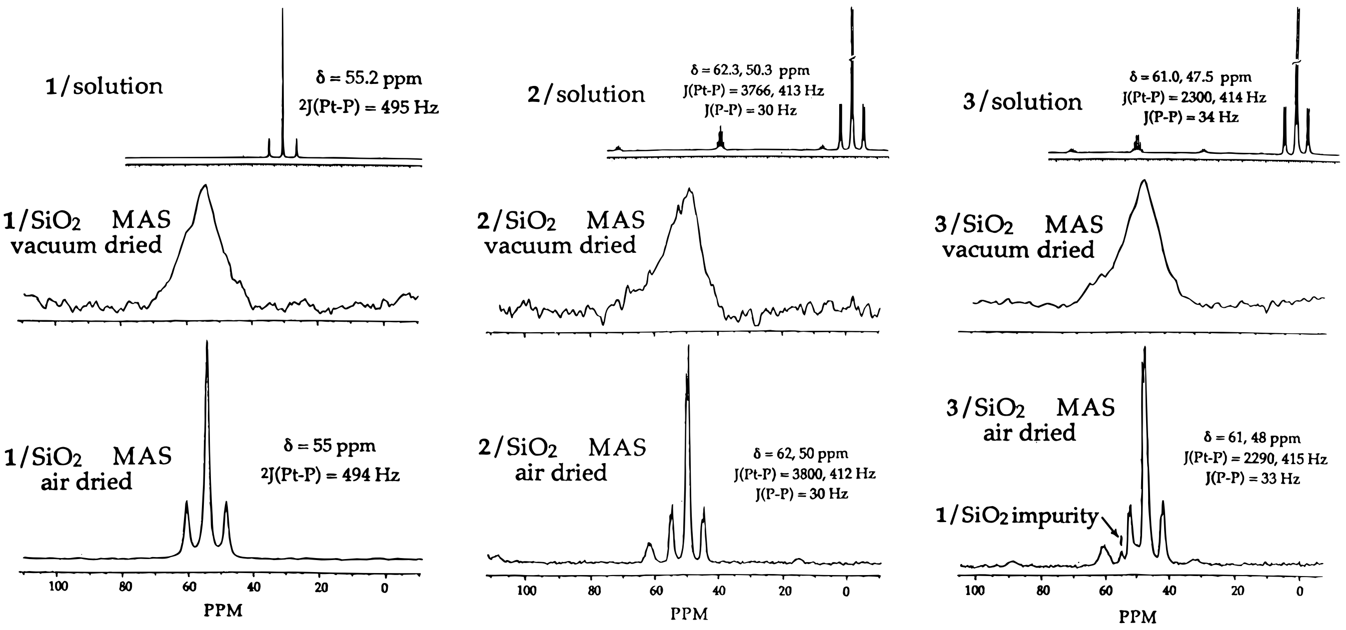

Figure 2. Proton-decoupled ^{31}P NMR spectra of the clusters $[Pt(AuPPh_3)_8](NO_3)_2$ (**1**), $[(PPh_3)Pt(AuPPh_3)_6](NO_3)_2$ (**2**), and $[(PPh_3)Pt(H)(AuPPh_3)_7](NO_3)_2$ (**3**): CH_2Cl_2 solution spectrum (202.35 MHz) and solid-state spectra of the clusters adsorbed on SiO_2 (air- and vacuum-dried) with magic angle spinning (40.53 MHz). The air-dried samples were exposed to the open atmosphere for not more than 10 min after removal of the CH_2Cl_2 solvent. The vacuum-dried samples were pumped on for 1 h.

of **1**, **2**, and **3** supported on SiO_2 (air-dried and vacuum-dried) are shown in Figure 2, along with their high-resolution CH_2Cl_2 solution spectra (121.4 MHz). Samples dried in air for about 10 min after removal of the CH_2Cl_2 solvent gave good resolution, enabling accurate determination of the chemical shifts (δ) and coupling constants. Vacuum drying resulted in significant line broadening; however, the chemical shifts did not change. Exposure of the vacuum-dried samples to CH_2Cl_2 and air drying for 10 min gave back the original spectra of the air-dried samples, showing that this change is reversible. The air-dried samples apparently retain enough solvent to give the clusters some molecular motion or mobility. This phenomenon has been observed previously for supported phosphine-ligated complexes.[20] The supported clusters could not be desorbed by washing with CH_2Cl_2 solution so they are indeed adsorbed on the supports, albeit with weak ion-pairing interactions. The solid state spectra of the air-dried samples gave δ, J_{P-Pt}, and J_{P-P} values that are within experimental error of values from solution spectra (Figure 2). Analogous results were obtained for the clusters **1** and **2** supported on Al_2O_3.[21] Samples of **1** and **2** supported on SiO_2 and Al_2O_3 that were heated at 135 °C under high vacuum and used in H_2-D_2 equilibration catalysis experiments at RT (see below) gave ^{31}P MAS NMR spectra that were identical to those described above. ^{31}P MAS NMR of samples of **3**/SiO_2 heated above ca. 50 °C showed the formation of some **1**/SiO_2 and **2**/SiO_2. Desorption of a heated sample of **3**/SiO_2 showed a mixture of **1** and **2** as determined by ^{31}P NMR analysis of the resulting solution. Samples of **3**/Al_2O_3 began decomposing even at RT, indicating that **3** is unstable on both supports.

The UV−visible spectra of the SiO_2-supported clusters were recorded as CH_2Cl_2 gel/suspensions and compared with their solution spectra. A comparison of the two spectra for **1** is shown in Figure 3. The close similarity of these spectra provides additional evidence that the supported clusters are intact without major changes in structure. Similar results were obtained for clusters **2**/SiO_2 and **3**/SiO_2. UV−visible diffuse reflectance spectra of the supported clusters also showed a close resemblance to the spectra recorded in solution.

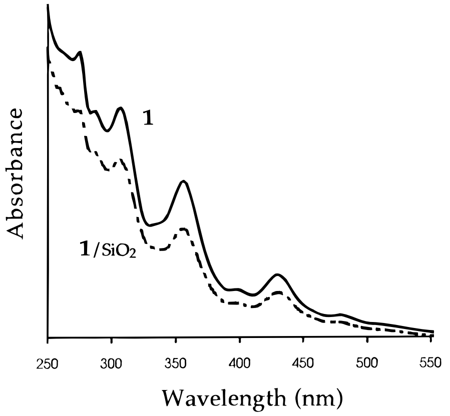

Figure 3. UV−visible absorption spectra of cluster **1** in CH_2Cl_2 solution and adsorbed on silica and of **1**/SiO_2 as a suspension in CH_2Cl_2 solvent (absorbance is arbitrary and adjusted to be on scale with the solution spectrum).

The CO adducts of **1** and **2** have characteristic ν(CO) stretching vibrations in the IR, and this can serve as a probe for changes in the cluster upon adsorption. The ν(CO) values for the supported CO adducts **1(CO)** and **2(CO)** are virtually identical to values obtained with solid samples of the molecular clusters. For example, FT-IR spectra of pressed wafers of **1-(CO)**/Al_2O_3 and **1(CO)**/SiO_2 gave ν(CO) values of 1941 and 1945 cm^{-1}, respectively, compared with 1943 cm^{-1} for a KBr wafer of the molecular cluster.[18] The supported clusters **1**/SiO_2 and **1**/Al_2O_3 also reacted cleanly with 1 atm of CO to form the supported CO adducts. This surface transformation was monitored by UV−visible and ^{31}P MAS NMR spectroscopy. Figure 4 shows the UV−visible spectral changes that occur after the addition of CO (1 atm) to **1** in CH_2Cl_2 solution and **1** supported on SiO_2. The changes are irreversible at RT. The results clearly show that the CO adduct forms on the support. ^{31}P MAS NMR spectra also showed that this transformation on the solid supports was clean. Similar results were obtained for cluster **2**.

The nature of the supported clusters was further probed by CO chemisorption (at RT) and TPD experiments. Cluster **1**

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(21) **2**/Al_2O_3: δ 49, $J_{P-Pt} = 4.1 \times 10^1$ and δ 60, $J_{P-Pt} = 3.7 \times 10^3$. **2**/$CH_2Cl_2$: δ 50, $J_{P-Pt} = 413$ and δ 62.3, $J_{P-Pt} = 3766$.

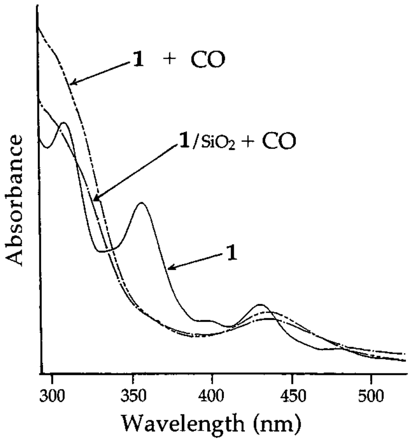

Figure 4. UV−visible absorption spectra of cluster **1** in CH_2Cl_2 solution and in CH_2Cl_2 solution after addition of CO, and **1**/SiO_2 after addition of CO.

was studied on Al_2O_3 and SiO_2 supports, and in both cases quantitative (1 CO per cluster) uptake of CO was observed. TPD of **1(CO)**/Al_2O_3 and **1(CO)**/SiO_2 gave quantitative CO desorption with peak maxima at about 70 °C. Chemisorption of CO for cluster **2** was only studied on SiO_2, and again quantitative CO uptake was observed. With **2(CO)**/SiO_2 the CO could be more easily removed by pumping, even at RT. This is consistent with observations in solution where CO is more labile for **2(CO)** than for **1(CO)**.[13,16,18] Chemisorption experiments were also carried out with H_2 for **1**/Al_2O_3 and **1**/SiO_2 with results that are very similar to those obtained for the molecular cluster **1**. In these experiments ca. 0.8 mol of H_2 was reversibly adsorbed per mol of supported **1** at 760 Torr and RT, in agreement with the known reaction $[Pt(AuPPh_3)_8](NO_3)_2 + H_2 \rightleftharpoons [Pt(H)_2(AuPPh_3)_8](NO_3)_2$.[15,16] The bound H_2 was rapidly removed by a He purge at RT. The reversible binding of H_2 to **1**/SiO_2 was also monitored by UV−visible spectroscopy. The spectral changes observed for a CH_2Cl_2 gel/suspension of **1**/SiO_2 upon treatment with 1 atm of H_2 were very similar to those carried out with a homogeneous CH_2Cl_2 solution of **1**.

Catalysis Studies. TOR's for H_2−D_2 equilibration were determined for the supported clusters with use of a flow reactor (see Experimental Section). The results are reported in Table 1. The rates are independent of support particle size (40−60 to 80−100 mesh), indicating that they are not limited by gas diffusion.[22] There was no induction period, and the rates remained constant for at least a day under H_2 at RT. Samples stored for up to several weeks also gave the same rates. The blank supports similarly pretreated or after cluster desorption were inactive for H_2−D_2 equilibration. The rates for **1** and **2** did not depend significantly on the support but were reproducible only after pretreatment at 135 °C under high vacuum. These clusters remained intact after this pretreatment and after H_2−D_2 equilibration catalysis (see above). We assume this thermal treatment was necessary to remove residual solvent and water. Samples of supported **1** and **2** evacuated at RT and not heated to 135 °C were less active by at least 50% and gave poor reproducibility. Cluster **3** was much less stable on the supports, and its rate is only reported for high-vacuum pretreatment at RT on SiO_2, where it remained intact. This cluster was significantly more active (TOR = 170 s^{-1}) than supported **1** and **2**. Pretreatment of **3**/SiO_2 at 135 °C resulted in a decrease in TOR to ca. 12 ± 1 s^{-1}, in agreement with its decomposition into a mixture of **1** and **2** (see above). This decomposition and loss of activity also occurred for **3**/Al_2O_3 at RT. The gold cluster $[Au(AuPPh_3)_8](NO_3)_3$ was supported on SiO_2 as a control and pretreated at RT under high vacuum. This cluster remained intact under these conditions (^{31}P MAS NMR and desorption) and was inactive for H_2−D_2 equilibration. A Pt/SiO_2 metal particle catalyst was prepared and was less active than **3**/SiO_2 and activated samples of **1**/SiO_2 (see below), showing the unexpected high activity of these supported, intact, molecular Pt−Au clusters.

Table 1. Rate Data for Catalytic H_2−D_2 Equilibration under Heterogeneous Conditions

compound	turnover rate (s^{-1}) for HD production[a]
$[Pt(AuPPh_3)_8](NO_3)_2$ (**1**)/Al_2O_3	12 ± 1
$[Pt(AuPPh_3)_8](NO_3)_2$ (**1**)/SiO_2	11 ± 1
$[(PPh_3)Pt(AuPPh_3)_6](NO_3)_2$ (**2**)/Al_2O_3	12 ± 2
$[(PPh_3)Pt(AuPPh_3)_6](NO_3)_2$ (**2**)/SiO_2	22 ± 2
$[(PPh_3)Pt(H)(AuPPh_3)_7](NO_3)_2$ (**3**)/SiO_2	170 ± 30[b]
$[Au(AuPPh_3)_8](NO_3)_3$/SiO_2	0 ± 0.05[c]
Pt/SiO_2[d]	100 ± 20
blank SiO_2 support[e]	0

[a] Turnover rates were determined at RT with partial pressures $P(H_2) = P(D_2) = 370$ Torr. Values for all supported clusters are given as (mol of HD)/(mol of cluster)(s) and for Pt/SiO_2 as (mol of HD)/(mol of active Pt)(s). The number of moles of active Pt was determined by irreversible CO chemisorption. The experimental error in turnover rate was estimated be repeating the experiment several times with freshly prepared samples and reported as the full range of measured values. [b] Pretreatment at RT. This cluster remained intact after H_2−D_2 equilibration catalysis at RT, but was irreversibly transformed into a mixture of **1** and **2** on the support by heating to 135 °C under vacuum (see text). [c] Pretreated at RT. [d] Pt metal was supported on the same silica by a standard procedure (0.1 wt % loading) as described in the Experimental Section. The sample was reduced at 400 °C under a H_2 flow just prior to catalysis. [e] Pretreatment of blank support was identical to that for the supported clusters.

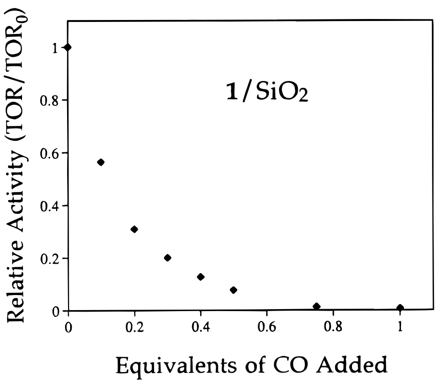

Figure 5. The effect of incremental additions of CO on the relative activity for H_2−D_2 equilibration with **1**/SiO_2 as catalyst. The relative activity is given as the ratio of the observed turnover rate (TOR) to the TOR without CO present.

The addition of a molar excess of CO to samples of **1**/Al_2O_3, **1**/SiO_2, or **2**/SiO_2, followed by a He purge to remove the nonadsorbed CO, resulted in the complete poisoning of H_2−D_2 equilibration catalysis. The catalytic activity was completely restored by high-vacuum treatment at 135 °C for 1 h. Desorption experiments showed only the presence of the original cluster. In the solution phase, freshly prepared **1(CO)** is inactive for H_2−D_2 equilibration, although some activity is observed as the CO slowly dissociates with time.[16] The adsorption of 0.1 equiv of CO/cluster molecule by **1**/SiO_2 resulted in a decrease in turnover rate of ca. 45%. Continued incremental additions of CO slowed the rate more gradually up to 1 equiv where the catalyst was inactive (Figure 5). This result is important and suggests that some of the supported clusters are more active than others. It also demonstrates that the catalysis is not caused

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by an irreversibly formed, highly-active, cluster fragmentation product too small for detection by analytical methods. These conclusions assume that the CO reacts more rapidly with the more active sites.

Clusters **1**−**3** also catalyze the hydrogenation of ethylene to ethane in solution and solid phases, but the rate is much slower than that for H_2−D_2 equilibration.[15] For example, in CH_3OH solution the TOR for **1** was ca. 5×10^{-5} s^{-1} (20 °C, $P(C_2H_4) = P(H_2) = 380$ Torr). The rate for **1** supported on Al_2O_3 or SiO_2 under the same conditions of temperature and pressure was ca. 2×10^{-3} s^{-1}. This rate can be compared to 1 s^{-1} determined under the same conditions for Pt/SiO_2 (corrected for the number of mol of active Pt). The number of moles of active Pt was determined by irreversible CO chemisorption. The lower activity for the intact molecular cluster **1** compared to that of small Pt particles is most likely due to the steric hindrance by the PPh_3 ligands bound to the Au atoms. A space-filling drawing of **1** showing the view with the largest access channel into the metal core is illustrated in the summary of this article on the Table of Contents page. H_2 and D_2 are small enough to enter this channel without difficulty, but the intact cluster may hinder access of the larger ethylene molecule.

Thermal Activation. Our long-range goal is to explore the use of preformed Pt−Au clusters as precursors to uniform, highly-dispersed Pt−Au particle catalysts on supports. We therefore have begun studying the thermal activation of **1**−**3** on oxide supports. The results of some preliminary experiments are given here. Cluster **3** on SiO_2 and Al_2O_3 is unstable to any heating and decomposes to give a mixture of **1** and **2** upon desorption. A thermolysis experiment with **1**/SiO_2 showed that the cluster remained intact (^{31}P MAS NMR) with heating under vacuum up to at least 180 °C. The TOR for the H_2−D_2 equilibration probe reaction was also determined for **1**/SiO_2 preheated for 1 h at various temperatures (temperature ramp ca. 10 °C/min under vacuum) and cooled to RT. This reactivity profile showed that the TOR remained constant at 11 ± 1 s^{-1} from 135 to 180 °C, decreased significantly to ca. 2 s^{-1} from 180 to 220 °C, and increased to values above 12 s^{-1} at 300 °C. This result indicates that the initial thermal decomposition of **1**/SiO_2 under vacuum leads to a decrease in H_2−D_2 equilibration activity. We have not yet studied the state of the clusters during thermolysis above 180 °C by spectroscopy or desorption. Pretreatment of **1**/SiO_2 and **2**/SiO_2 by heating under a H_2 flow yielded catalysts with significantly higher RT activities for H_2−D_2 equilibration. Reactivity profiles showed that maximum and reproducible TOR's were obtained for heating under H_2 at 110 °C for 25−50 min for **1**/SiO_2 and for 10−25 min for **2**/SiO_2 (heating from RT was carried out under vacuum with a ramp of 10 °C/min). The TOR's measured for these catalysts at RT were 220 ± 20 and 85 ± 10 s^{-1} for **1**/SiO_2 and **2**/SiO_2, respectively. Shorter or longer heating times under H_2 gave lower TOR's. Characterization of these samples by ^{31}P NMR on the support (MAS) and after desorption (solution) showed that the clusters were intact without measurable decomposition. Thermolysis under H_2 at 135 °C for more than several minutes resulted in significantly lower TOR's. The maximum TOR observed for **1**/SiO_2 after heating under H_2 as described above is comparable to the TOR observed for **3**/SiO_2 without any heating. This observation has mechanistic implications (see below). It is also important to note that thermolysis under vacuum or H_2 at slightly higher temperatures or for prolonged periods of time resulted in decreased TOR's. Higher TOR's were only achieved after heating at considerably higher temperatures (>300 °C) where metal particles presumably begin to form. The effect of thermolysis at higher temperatures is under current investigation.

Conclusions and Comments on the Mechanism of Heterogeneous H_2−D_2 Equilibration Catalysis. Clusters **1** and **2** on SiO_2 and Al_2O_3 supports are intact and gave TOR's for H_2−D_2 equilibration (Table 1) that are in reasonable agreement with rates measured for solid, microcrystalline samples of the molecular clusters.[16] The rates are much greater than in homogeneous solution phase primarily due to the low solubility of H_2 in organic solvents. The TOR's for these clusters on SiO_2 significantly increased (by a factor of 20 for **1**/SiO_2) after heating at 110 °C under H_2, although ^{31}P MAS NMR showed no significant changes and desorption indicated no irreversible transformations. The supports were also inactive after desorption. The most reasonable explanation for this observation is that the rigid oxide support promotes the partial dissociation of a PPh_3 ligand from the 18-electron, dihydrido cluster **1(H)$_2$** or **2(H)$_2$**, thus stabilizing species with a bare Au atom. A reversible ligand dissociation step has been strongly implicated by kinetic experiments in the mechanism for H_2−D_2 equilibration in homogeneous solution phase (see steps 1−3 in the Introduction).[16,19] Ligand exchange measurements in solution by ^{31}P NMR showed that 16-electron clusters **1** and **2** undergo facile phosphine exchange with free tri-*p*-tolylphosphine *only* in the presence of H_2, implying the necessity to form the 18-electron dihydride. Exchange did not occur under a N_2 or air atmosphere. This is consistent with the need for H_2 to "activate" the supported clusters by forming dihydride species. Thermolysis under vacuum even at 220 °C did not increase the TOR of the supported clusters. The fact that **3**/SiO_2 is highly active (TOR = 170 s^{-1}) without thermolysis under H_2 is also consistent with a PPh_3 dissociation mechanism. This compound is already an 18-electron cluster and shows facile ligand exchange in solution under N_2 or air atmosphere.[19] The support-promoted, partial PPh_3 dissociation, therefore, can occur without the need for thermolysis under H_2.

It is disappointing that ^{31}P MAS NMR did not show evidence of a dissociated or partially dissociated PPh_3 ligand for any of the supported clusters, including samples of **1** and **2** on SiO_2 that were activated by heating under H_2 at 110 °C. Desorption experiments also showed that no irreversible changes in these clusters occurred, but such experiments are obviously unable to reveal reversible changes on the support. The ^{31}P MAS NMR of the air-dried samples where good resolution was achieved (Figure 2) gave no evidence of resonances due to free or support bound PPh_3. Since the air-dried samples contain some residual CH_2Cl_2 solvent and have increased mobility (see above), it is possible that a partially dissociated PPh_3 reattaches to a Au atom upon exposure to solvent. These "wet" samples were also significantly less active for H_2−D_2 equilibration than vacuum/heat-dried or H_2/heat-activated samples. A CO incremental poisoning experiment with 110 °C/H_2 treated **1**/SiO_2 showed a distribution of activated clusters similar to that illustrated in Figure 5. Spectroscopic detection of a small fraction of clusters with a partially dissociated PPh_3 would be very difficult indeed, especially with the lower resolution of the ^{31}P MAS NMR of vacuum-dried samples. These results vividly demonstrate the importance of using the rate of a probe reaction to study supported catalysts.

It is worth noting that a similar support-promoted activation of an *intact* molecular cluster on silica has been reported.[3] The cluster $Ru_3(CO)_6[1,2\text{-}(\mu\text{-}PPh)_2C_6H_4]_2$ supported on Cab-o-sil was significantly activated for the hydrogenation and isomerization of 1-octene in comparison to the reaction under homogeneous conditions. It was concluded that the support in some way activated the cluster so that the required open coordination site is created without the irreversible loss of a ligand or cluster fragmentation.[3] It is unwarranted to speculate further about the mechanism of such activation processes as more data is obviously needed. Some experiments currently being carried out with supported Pt−Au clusters include the following: (a) variation of anion, phosphine ligand, deposition procedure, and support; (b) TEM, EXAFS, and microprobe analysis; (c) thermolysis at higher temperatures. The results of this current study have advanced our knowledge of M−Au cluster chemistry with respect to stability in an oxide support environment, methods of spectroscopic characterization in the solid-state, and mechanism of H_2 activation catalysis in general and on a support.

Experimental Section

Sample Preparation and Spectroscopic Analysis. The cluster compounds **1**−**3** and $[Au(AuPPh_3)_8](NO_3)_3$ were prepared according to literature procedures and characterized by $^{31}P\{^1H\}$ NMR and UV−visible spectroscopy in solution.[9,12,18,23,24] The cluster compounds were at least 98% pure. The supports (Criterion γ-Al_2O_3, surface area = 200 m^2/g; Davisil SiO_2, surface area = 360 m^2/g, average pore diameter = 150 Å) were sieved into 40−60, 60−80, and 80−100 mesh ranges, washed with high-purity water (distilled and deionized) to remove the fines, and heated under vacuum at 120 °C for 24 h to remove surface H_2O. The procedure for cluster deposition on the supports and pretreatment of the supported cluster samples are described in the text. The pretreatment procedures used should not lead to significant dehydroxylation of the supports. Catalyst pretreatment, characterization (BET, chemisorption, and TPD), and rate measurements were carried out with use of an RXM-100 catalyst characterization and gas-handling system (Advanced Scientific Designs, Inc.). Solid-state ^{31}P MAS NMR spectra were recorded at 40.53 MHz with use of a Bruker AC-100 spectrometer with proton decoupling and a spinning speed of ca. 3 kHz. Cross-polarization was used for the vacuum-dried samples but not for the air-dried samples. $^{31}P\{^1H\}$ NMR solution spectra were recorded at 202.35 MHz with use of a Varian VXR-500 spectrometer. All chemical shifts are reported relative to trimethyl phosphate with positive shifts downfield. Triphenylphosphine was used as an external reference for the solid-state experiments with $\delta = -11.9$ ppm. UV−visible spectra were recorded with use of a Hewlett-Packard (Model 98155A) spectrometer. Samples of clusters supported on silica were run as gel/suspensions in CH_2Cl_2 solvent with a suspension of SiO_2 used as a reference. The reflectance spectra were recorded with use of a Model 8452A HP spectrometer equipped with an integrating sphere (Labsphere RSA-HP-84 reflectance spectroscopy accessory). Infrared spectra were recorded with use of a Mattson FTIR (Sirius 100) spectrometer. For supported clusters, the pure support was first pressed into a thin wafer and the spectrum recorded for background subtraction. The cluster was then adsorbed as usual from CH_2Cl_2 solution on the same wafer, washed with CH_2Cl_2 solvent, air-dried, and subjected to IR analysis. Subtraction of the pure support was necessary for good spectra. Spectra were recorded at 4 cm^{-1} resolution.

Preparation of Pt/SiO_2. Metallic Pt particles were deposited on the same Davisil SiO_2 support (pretreated as described above) by a literature procedure that involved adsorption of $[Pt(NH_3)_4](NO_3)_2$ (Strem) from aqueous solution at pH 9, calcination in O_2 at 300 °C for 30 min, and reduction under H_2 at 400 °C for 3 h.[25] The sample used had a Pt loading of 0.1% (w/w). TOR values determined with this catalyst were corrected for the fraction of Pt atoms exposed as determined by CO chemisorption.[26] The catalyst samples had dispersions in the range of 50−60%.

CO and H_2 Uptake Measurements. Carbon monoxide uptake at RT for supported samples of **1** and **2** was determined using a volumetric, two-isotherm experiment. The total CO adsorption isotherm was measured for the supported cluster over a pressure range of 20−80 Torr. A second adsorption isotherm was measured for the blank support over the same pressure range. The CO adsorption by the cluster was calculated by subtraction of the second isotherm from the first.[26] This procedure was necessary due to the reversible nature of CO binding to the supported clusters. Quantitative CO uptake was found for both supported clusters. The uptake of H_2 was more difficult to measure for **1**/SiO_2 because the reaction is reversible and not complete below 1 atm at RT. The same procedure as described for CO was used but over the pressure range 20−100 Torr. The data have a larger error than that for CO, and extrapolation to 760 Torr is problematic. The results showed that the percent of uptake (mol of H_2/mol of **1**) was 48 ± 2% at 80 Torr and 77 ± 10% at 760 Torr (by extrapolation), in fair agreement with previous measurements for molecular solids and solutions of **1**.[15,16]

Temperature-Programmed Desorption of CO. TPD analyses were carried out on samples of **1** on SiO_2 and Al_2O_3 supports after exposure to CO at 1 atm. The sample (250 mg) was placed in a quartz U-shaped microreactor and evacuated at ambient temperature until a base pressure of 1.0×10^{-7} Torr was reached. The sample was then heated linearly from 30 to 150 °C at a temperature ramp of 5 °C/min with direct evacuation of desorbed gases into a chamber containing a UTI 100c quadrupole mass spectrometer. Mass 28 was monitored and quantified (by precalibration) as a function of temperature.

H_2−D_2 Equilibration TOR. Turnover rates for H_2−D_2 equilibration were calculated from the measured percent conversion for the reaction $H_2 + D_2 \rightleftharpoons 2HD$ in the effluent from a flow reactor containing a known amount of catalyst (typically ca. 100 mg) and the flow rate of H_2 and D_2. The details of this calculation are given in ref 27. The flow rate of the reactant gases was always the same and controlled to within ± 0.1 cm^3 min^{-1} with use of electronic mass flow controllers. Total flow rates were varied between 10 and 100 cm^3 min^{-1} to keep the percent conversion between 5 and 15%. Under these conditions the conversion to HD was linearly dependent on the flow rate. The rates also did not depend on support particle size (vide infra). The effluent gas was analyzed with a Leybold Inficon Quadrex 200 mass spectrometer tuned and calibrated to give accurate relative amounts of H_2, HD, and D_2. The H_2 and D_2 reactant gases were purified by passage through liquid N_2 traps.

Ethylene Hydrogenation TOR. A mixture of ethylene and H_2 gas (equal pressures) was recirculated (50 cm^3 s^{-1}) through a flow reactor in a closed loop (ca. 31 cm^3 total volume of loop and reactor) at RT and 1 atm total pressure. The flow reactor contained 250−500 mg of the catalyst. Gas samples (0.1 cm^3) were periodically extracted via an automatic gas-sampling valve and injected into a flowing He stream for analysis by gas chromatography. Relative amounts of ethylene and ethane were determined from the integrator (Model 3393A) of a HP 5890A GC equipped with a Porapac Q (80/100) column and TCD detector. TOR's were calculated are on the basis of the initial rate for ca. 3% conversion to ethane.

Incremental CO Poisoning. Catalyst samples of **1**/SiO_2 were poisoned with fractional equivalents of CO by injection of 0.1 cm^3 increments of CO at the appropriate pressure (via an automatic gas-sampling valve) into a loop of recirculating He gas (800 Torr) containing the sample at RT. The gas mixture was allowed to circulate for 0.5 h, after which the sample was evacuated and the H_2−D_2 equilibration TOR determined as described above. The results of incremental poisoning experiments did not vary with increasing the recirculation times up to 4 h.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-9222411) and by the University of Minnesota. M.E.C. is the recipient of a University of Minnesota Undergraduate Research Opportunities grant. M.B.C. is a participant in the University of Minnesota, Department of Chemistry NSF-REU/Lando Undergraduate Summer Research program.

IC9504147

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