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[12] a) Crystal structure analysis of **1**. A single crystal with dimension of 0.25 × 0.15 × 0.05 mm was coated with a sealing material and mounted on a glass fiber. All measurements were made on a Rigaku RAXIS Rapid IP detector equipped with a graphite monochromated $Mo_{K\alpha}$ radiation source. The data were collected at 293(2) K. The crystallographic molecule contains half a molecule of **1**. Crystal data: $C_{42}H_{48}N_{18}O_{18}Pd_3 \cdot 2H_2O$, $M_r = 1448.13$; orthorhombic, space group *Pmn*21, $a = 21.8807(4)$, $b = 14.7319(3)$, $c = 23.2315(2)$ Å, $V = 7488.5(2)$ Å^3, $\rho_{calcd} = 1182\ kg\,m^{-3}$. $Z = 8$, $F(000) = 2696$, $\mu(Mo_{K\alpha}) = 7.68\ mm^{-1}$, $\lambda = 0.71073$ Å. 19837 reflections measured, 7874 observed reflections ($I > 2\sigma(I)$); number of parameters 648; $R_1 = 0.1197$; $wR_2 = 0.3421$. Further refinement was unsuccessful because of the high degree of disorder of the counter anions and the water molecules. b) CCDC-191629 (**1**) and CCDC-191630 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[16] Crystal structure analysis of **2**. A single crystal with dimension of 0.25 × 0.15 × 0.05 mm was coated with a sealing material and mounted on a glass fiber. All measurements were made on a Rigaku RAXIS Rapid IP detector equipped with a graphite monochromated $Mo_{K\alpha}$ radiation source. The data was collected at 293(2) K. The crystallographic molecule contains a molecule of **2**. Crystal data: $C_{66}H_{48}N_{18}O_{18}Pd_3 \cdot 2H_2O$, $M_r = 1736.40$, monoclinic, space group *C*2/*c*, $a = 39.366(8)$, $b = 24.887(5)$, $c = 18.217(4)$ Å, $\beta = 106.69(3)°$, $V = 17095(6)$ Å^3, $\rho_{calcd} = 1.544\ kg\,m^{-3}$, $Z = 32$, $F(000) = 8192$, $\mu(Mo_{K\alpha}) = 0.902\ cm^{-1}$, $\lambda = 0.71073$ Å; 19127 reflections measured, 7704 observed reflections ($I > 2\sigma(I)$); number of parameters 891; $R_1 = 0.0931$; $wR_2 = 0.2575$.[12b]

Supported Gold Catalysts

Structure and Reactivity of a Mononuclear Gold-Complex Catalyst Supported on Magnesium Oxide[**]

Javier Guzman and Bruce C. Gates[*]

Oxide- and zeolite-supported mononuclear metal complexes are important industrial catalysts, for example, for alkene polymerization,[1] and some have properties not anticipated by known homogeneous catalysis.[2] Some supported transition-metal complexes are close analogues of molecular complexes, with the metal–support-oxygen bonds being as strong as metal–ligand bonds in common transition-metal complexes and strong enough to maintain anchoring during catalysis.[3]

Mononuclear gold complexes are used frequently in organometallic chemistry[4] and have been identified as catalysts for reactions including the addition of alcohols to alkynes,[5] asymmetric aldol reactions,[6] C–C bond formation,[7] oxidative carbonylation of amines,[8] and selective hydrosilylation of aldehydes.[9] Supported gold catalysts have recently been found to be surprisingly active and selective, for example, for CO oxidation and propene epoxidation.[10] Their unique properties have been variously attributed to the smallness of the gold clusters[10b] and to clusters adjacent to cationic gold species at the support surface.[11] Gold supported

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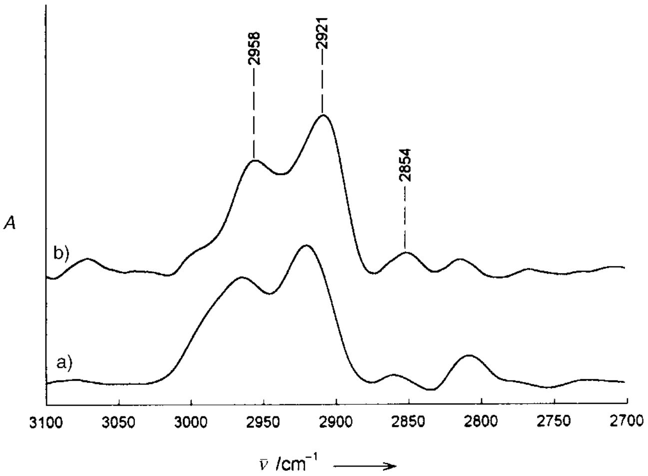

Figure 1. Infrared spectra in the ν_{CH} stretching region characterizing solid samples **2** (a) and **1** (b).

on SiO_2, Al_2O_3, or TiO_2 was observed to catalyze alkene hydrogenation,[12] and it was suggested that small gold clusters were the catalytically active species. However, the suggestion is unconfirmed, and, furthermore, there is a report[13] that the addition of gold to oxides makes the oxides even less active catalysts for ethene hydrogenation. The catalytic sites remain to be identified.

Herein we report the preparation and characterization of the first structurally simple supported gold complex, $[Au(CH_3)_2\{OMg\}_2]$ (**1**) (where the braces denote ligands that are part of the MgO surface) and show that it is a precursor of a mononuclear gold complex that catalyzes ethene hydrogenation. To test the catalytic activity of supported gold in various forms, we also prepared a family of small gold clusters[14] on the MgO support.

Adsorption of $[Au^{III}(CH_3)_2(acac)]$ (**2**; acac = acetylacetonate, $C_5H_7O_2$)[15] on MgO led to the formation of supported $Au(CH_3)_2$ species **1**, as shown by the IR bands (Figure 1) in the ν_{CH} region at 2958, 2854, and 1464 cm^{-1} (not shown), which nearly match those representing the CH_3 groups in solid **2**.[16] Furthermore, the changes in the ν_{OH} and ν_{COO} regions of the IR spectra characterizing **1** relative to those of bare MgO and of crystalline **2** indicate reaction of surface hydroxy groups of MgO and conversion of acac ligands, respectively, which results from the adsorption of **2**. The adsorption was confirmed by an increase in the intensity of the bands associated with hydrogen-bonded hydroxy groups (3689 and 3606 cm^{-1}) and a decrease in the intensity of bands associated with isolated hydroxy groups (3765 and 3749 cm^{-1}; Table 1).[17] The bands in the ν_{COO} region were shifted to higher frequencies and changed in intensity relative to those of solid **2**; moreover, new bands attributed to carbonaceous species, such as acetylacetone ($C_5H_8O_2$; 2921, 1708, and 1626 cm^{-1}), inferred to be formed during decomposition of **2**, were observed for **1** (Table 1). Thus, we infer release of the acac ligand from the gold center and its decomposition during adsorption of **2**.[18] The IR data suggest ligand exchange of the acac ligand with support oxygen atoms (basic surface sites, O^{2-} ions) and hydrogen-bonding of surface OH groups to the organic moiety, facilitating the formation of **1**.

Table 1: Infrared spectra representing samples **1** and **2**.

Sample	IR bands [cm^{-1}]
1	3765, 3749, 3689, 3606, 2958, 2854, 2921, 1708, 1626, 1517, 1464, 1420, 1285
2	2959, 2923, 2860, 1586, 1531, 1463, 1390, 1285

Other metal complexes containing nucleophilic ligands, such as acac, have also been shown to bond to metal-oxide surfaces by hydrogen bonding to hydroxy groups and by exchange of the ligands with support oxygen atoms.[3,19] The acid–base pair sites on a support surface may initiate an acid–base catalyzed decomposition of the complex as it comes in contact with the surface and releases the ligand to be replaced by a group from the surface, such as $\{OMg\}^{-1}$.[17,19] Ligand-exchange reactions of comparable metal complexes in solution (e.g., $[Pt(acac)_2]$ and $[Pd(acac)_2]$) have also been reported.[20]

The X-ray absorption near-edge spectrum (XANES) characterizing **1** is virtually identical to that characterizing crystalline **2**. This comparison indicates that the gold retained its oxidation state of +III after the chemisorption of **2** (in which Au^{III} is bonded to $C_5H_7O_2$ through two oxygen atoms[21]).

Extended X-ray absorption fine structure (EXAFS) results characterizing **1** (measured at the Au L_{III} edge, 11919 eV, Table 2), show that in the surface complex the gold center was also bonded to two oxygen atoms. These are inferred to be part of the MgO surface (although the exact bonding sites are unknown), because the Au–O separation was found to be 2.16 Å (vs. 2.08 Å in **2**[21]), typical of M–O bonding distances in other zeolite- and oxide-supported mononuclear metal complexes (e.g., $[Rh(CO)_2\{OAl\}\{OSi\}]$ (supported on highly dealuminated zeolite Y), 2.15 Å;[3b] $[Ru(CO)_2\{OAl\}_2]$ (on γ-Al_2O_3), 2.17 Å;[22] and $[Re(CO)_3\{OMg\}\{HOMg\}_2]$ (on MgO), 2.13 Å[3a,23]). Another Au–O contribution in the EXAFS spectrum of **1** was found at a nonbonding distance of 2.85 Å (with a coordination number

Table 2: EXAFS parameters characterizing **1** and the species formed from it during ethene hydrogenation catalysis.[a]

Sample	Shell	N	R [Å]	$10^3 \times \Delta\sigma^2$ [$Å^2$]	ΔE_0 [eV]
1	Au-Au	–[b]	–	–	–
	Au-O_s	2.1	2.16	0.20	3.45
	Au-O_l	0.9	2.85	1.04	1.02
	Au-Mg	0.9	2.72	1.45	1.35
	Au-C	2.0	2.04	2.35	2.57
Working catalyst[c]	Au-Au	–[b]	–	–	–
	Au-O_s	2.0	2.18	2.14	2.34
	Au-O_l	0.9	2.87	3.13	4.62
	Au-Mg	0.9	2.73	2.46	3.17
	Au-C	–[b]	–	–	–

[a] Notation: N = coordination number; R = distance between absorber and backscatterer atoms; $\Delta\sigma^2$ = Debye–Waller factor; ΔE_0 = inner potential correction. The subscripts s = short and l = long. Typical errors are as follows: $N \pm 10\%$, $R \pm 0.02$ Å, $\Delta\sigma^2 \pm 20\%$, $\Delta E_0 \pm 20\%$. [b] Undetectable. [c] Catalytic reaction conditions stated in the Experimental Section.

of 0.9), along with another (weak) contribution tentatively identified as Au–Mg ($N = 0.9$, 2.72 Å). The data also show a weak Au-C contribution ($N = 2.0$) at a distance of 2.04 Å (vs 2.05 Å in **2**[21]) that confirms the bonding of two carbon atoms to the gold center. The EXAFS data give no evidence of Au–Au contributions, consistent with the presence of site-isolated **1** on the MgO surface.

The catalytic activity[24] of the species formed from **1** and its stability in operation in a flow reactor were tested for hydrogenation of ethene. After a break-in period of about 30 min for attainment of steady state, the activity (measured at conversions less than 5%) was found to be unchanged during the measurements (12 h), corresponding to a reaction rate (determined from differential conversion data) of 2.9×10^{-3} molecules of ethene converted (Au atom)$^{-1}$ s^{-1}.

The reaction was also carried out under the same conditions when the reactor was an X-ray absorption cell[25] which allowed collection of spectra of the working catalyst. The spectra were unchanged during the period of steady-state operation, which confirmed the stability of the catalyst. The data (Table 2) identify mononuclear gold species, with no evidence of gold clusters (as shown by the absence of detectable Au–Au contributions). The oxidation state of the gold was found by XANES to be +III.[26] The EXAFS data show that the Au^{III} center was bonded to two oxygen atoms of the MgO unit with an Au–O bond of 2.18 Å. The data did not indicate any Au–C contribution, which demonstrates the removal of the CH_3 ligands before or during catalysis.[27]

IR data were collected during pretreatment of the catalyst in flowing ethene or H_2 and also during catalysis. After **1** had been treated in H_2 (at 1 bar and 300 K), the IR spectra did not show any evidence of CH_3 ligands bonded to the gold centers, consistent with the EXAFS results (data not shown). The IR spectra are not sensitive enough to determine whether gold hydride formed, and we do not rule out the possibility.[28] The IR spectra also show that ethene interacts with **1** (at 1 bar and 300 K) to form only physisorbed ethene. During steady-state ethene hydrogenation catalysis, supported mononuclear gold complexes were characterized by their IR bands (not observed with the catalyst in contact with H_2 or ethene alone) at 3085, 2961, 2920, and 2870 cm^{-1}, which suggest the formation of ethene-derived adsorbates (ligands) on the gold center. When H_2, ethene, or a catalytically reacting mixture of H_2, ethene, and He interacted with the MgO support without gold, no ethene-derived ligands were observed (the adsorption was negligible). Thus, the data are consistent with the inference that the mononuclear gold complexes are themselves the catalytically active species. Individual ligands on the gold centers observed by IR spectroscopy during steady-state ethene hydrogenation were characterized by varying the reaction conditions[26] and comparing against published spectra.[29] The 2961, 2920, and 2870 cm^{-1} bands suggest the formation of ethyl ligands on the gold, consistent with the IR bands characterizing ethyl on metal surfaces[29a,b,c] and with CH_3CH_2Cl.[29d] The 3085 cm^{-1} band is consistent with the formation of π-bonded ethene, as observed for Pt, Pd, Ir, and Rh complexes.[30]

The results point to supported mononuclear Au^{III} complexes as the catalytically active species for ethene hydrogenation. To test whether supported gold clusters might be catalysts for this reaction, catalysis experiments were also performed with a family of MgO-supported samples containing gold clusters of various sizes (made by adsorption of **2** on MgO, followed by treatment in flowing He at increasing temperatures).[14] The catalytic activity for ethene hydrogenation decreased as the Au–Au coordination number (thus, the average cluster size[31]) characterizing the gold clusters in the catalysts prior to use increased (Figure 2). The data imply that large gold particles are not catalysts for ethene hydrogenation, and the highest activity was observed for the sample containing only mononuclear gold complexes.

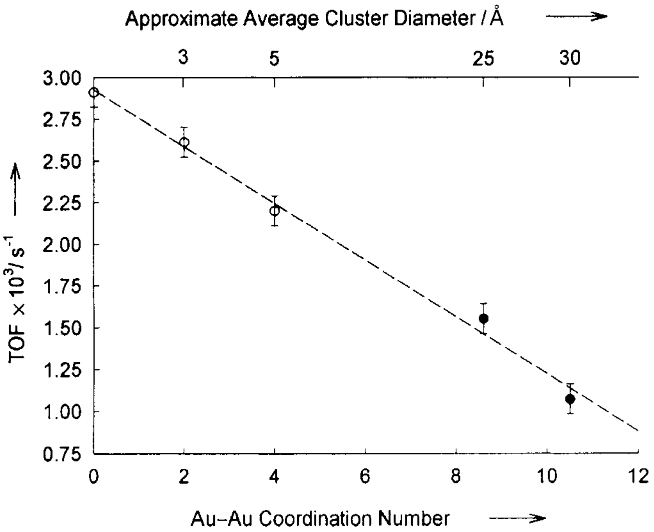

Figure 2. Activities of MgO-supported catalysts containing cationic gold and (except in the most active catalyst) gold clusters. Reaction conditions stated in Experimental Section. Note the nonlinearity of the scale at the top. XANES data were collected for the catalysts denoted by open symbols

XANES data indicate the presence of Au^{III} along with gold clusters in all the catalysts except the most active one, which contained Au^{III} complexes without detectable clusters. Thus, all the data are consistent with the inference that the catalytically active species in all the samples were mononuclear Au^{III} complexes; there is no evidence of the catalytic activity of gold clusters for ethene hydrogenation, consistent with the conventional wisdom about the lack of activity of samples containing zerovalent gold.[10b]

Experimental Section

The synthesis and sample handling were performed under anaerobic and anhydrous conditions. The MgO-supported gold complexes, containing 1 wt% Au, were prepared by slurrying **2** in dry and deoxygenated *n*-hexane with partially dehydroxylated MgO powder (pretreated at 673 K in vacuum; BET surface area 60 m^{2}g^{-1}). The slurry was stirred for one day and the solvent removed by evacuation.

Transmission IR spectra of the solid samples were recorded with a Bruker IFS 66v spectrometer operated with a spectral resolution of 4 cm^{-1}. Samples were pressed into self-supporting wafers and loaded into a cell (In-situ Research Institute, Inc., South Bend, IN) in a drybox. The cell was connected to a vacuum/adsorption system with a base pressure of 1.334×10^{-7} bar, which allowed recording of spectra while the treatment gases flowed through and around the wafer at temperatures ranging from room temperature to 573 K.

The X-ray absorption experiments were performed on beamline 4-1 of the Stanford Synchrotron Radiation Laboratory (SSRL) at the Stanford Linear Accelerator Center, Stanford, CA, and on beamline X-11A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, Upton, NY. The storage-ring electron energy was 3 GeV at SSRL and 2.5 GeV at NSLS; and the ring current varied within the range of 50–100 mA at SSRL and 140–240 mA at NSLS. The sample handling was as described elsewhere.[14] Data were recorded at the Au L_{III} edge (11919 eV) during ethene-hydrogenation catalysis and also with the catalyst in flowing He, H_2, or C_2H_4 at atmospheric pressure and 353 K. Higher harmonics in the X-ray beam were minimized by detuning the Si(220) monochromator at SSRL or the Si(111) double-monochromator at NSLS by 20–25% at the Au L_{III} edge.

The catalytic activity[24] and stability of species formed from **1** were tested for the hydrogenation of ethene by contacting a mixture of He, ethene, and H_2 (ethene partial pressure, P_{ethene}, 0.0533 bar, P_{hydrogen}, 0.2134 bar, the balance He) with **1** in a flow reactor at 1.0135 bar, and 353 K.

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