Rh₂**Cl**₂(**CO**)₄ adsorbed and tethered on gold powder: **IR** spectroscopic characterization and olefin hydrogenation activity

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Abstract: Catalysts were prepared by adsorbing $Rh_2Cl_2(CO)_4$ directly on gold powder or on gold that contained the tethered ligands 2-(diphenylphosphino)ethane-1-thiol (DPET) or methyl 2-mercaptonicotinate (MMNT). Infrared (IR) studies (diffuse reflectance infrared Fourier transform (DRIFT)) of the catalyst Rh–Au prepared by adsorbing $Rh_2Cl_2(CO)_4$ directly on Au indicate that a $Rh^I(CO)_2$ species is present. IR studies of Rh–DPET-Au suggest that tethered *cis*-Rh(DPET)(CO)_2Cl is the major species at relatively high $Rh_2Cl_2(CO)_4$ loadings, but *trans*-Rh(DPET)_2(CO)Cl is observable at low $Rh_2Cl_2(CO)_4$ loadings. Spectral investigations of the catalyst Rh–MMNT-Au prepared by adsorbing $Rh_2Cl_2(CO)_4$ on MMNT-Au suggest that tethered [*cis*-Rh(MMNT)_2(CO)_2]+Cl⁻ and (or) Rh(MMNT)(CO)_2Cl are the major species at low $Rh_2Cl_2(CO)_4$ loadings, while a new unidentified species predominates at high $Rh_2Cl_2(CO)_4$ loadings. All three catalysts are active 1-hexene hydrogenation catalysts under the mild conditions of 40°C and 1 atm of H₂; they are much more active than Au powder or $Rh_2Cl_2(CO)_4$ in solution. Of the three catalysts, Rh–Au is the most active with a maximum turnover frequency (TOF) of 800 mol H₂ per mol Rh per min while its turnover (TO) is 29 600 mol H₂ per mol Rh during a 2-hour run. Under the conditions of 1-hexene hydrogenation, the catalysts lose their CO ligands. Thus, it appears that a form of Rh metal on Au is the catalytically active species.

Key words: catalysis, olefin hydrogenation, gold powder, tethered rhodium complexes, infrared studies, adsorption, rhodium complexes.

Résumé : On a préparé les catalyseurs mentionnés dans le titre en faisant absorber du $Rh_2Cl_2(CO)_4$ directement sur de l'or en poudre ou sur de l'or qui contient les ligands fixés 2-(diphénylphosphino)éthane-1-thiol (DPET) ou 2mercaptonicotinate de méthyle (MMNT). Des études infrarouges («DRIFT») du catalyseur (Rh–Au) préparé par adsorption de $Rh_2Cl_2(CO)_4$ directement sur de l'or indiquent la présence d'une espèce $Rh^I(CO)_2$. Les études IR du Rh–DPET-Au suggèrent que, pour des chargements relativement élevés de $Rh_2Cl_2(CO)_4$, le *cis*-Rh(DPET)(CO)_2Cl est l'espèce fixée principale; on peut toutefois observer la formation de *trans*-Rh(DPET)_2(CO)Cl avec des chargements faibles de $Rh_2Cl_2(CO)_4$. Des études spectrales du catalyseur (Rh–MMNT-Au) préparé par adsorption de $Rh_2Cl_2(CO)_4$ sur du MMNT-Au suggèrent que, pour des chargements faibles de $Rh_2Cl_2(CO)_4$, le *[cis*-Rh(MMNT)_2(CO)_2]⁺Cl⁻ et (ou) le Rh(MMNT)(CO)_2Cl sont les espèces fixées principales; toutefois, pour des chargements élevés de $Rh_2Cl_2(CO)_4$, l'espèce principale est une nouvelle espèce qui n'a pas été identifiée. Les trois catalyseurs sont des catalyseurs actifs pour l'hydrogénation de l'hex-1-ène dans des conditions douces, soit 40°C et 1 atm. de H₂; en solution, ils sont beaucoup plus actifs que l'or en poudre ou le $Rh_2Cl_2(CO)_4$. Des trois catalyseurs, le Rh–Au est le plus actif avec une valeur maximale de "TOF" de 800 mol H₂/mol Rh-min alors que son "TO" est de 29,600 mol H₂/mol Rh pour une expérience de deux heures. Dans les conditions d'hydrogénation de l'hex-1-ène, les catalyseurs perdent leurs ligands CO. Il semble donc que l'espèce catalytiquement active soit une forme métallique de Rh sur de l'or.

Mots clés : catalyseur, hydrogénation d'oléfines, poudre d'or, complexes de rhodium fixés, études infrarouges, complexes de rhodium.

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Introduction

Heterogenized transition-metal complex catalysts, which offer distinct advantages over their homogeneous counterparts, have been extensively studied in the past few decades (1). Much work in this area has been dedicated to tethering organometallic complexes to insoluble organic polymers or inorganic oxides (2). Little information, however, has been reported on transition-metal complexes tethered to metallic surfaces (3).

The adsorption of organic molecules on solid metal surfaces has been extensively studied in recent years (4). Gold

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Dedicated with best wishes to Professor Brian James on the occasion of his 65th birthday.

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metal has been investigated extensively because it does not form a surface oxide under atmospheric conditions at room temperature (5, 6). Among the organic compounds (7, 8) that adsorb on gold are thiols (RSH) and disulfides (RSSR), which produce RS groups on the surface (9). For example, terminal alkyl thiols, $X(CH_2)_nSH$ ($n \ge 1$ and X = COOH, $CONH_2$, CN, CH_2NH_2 , etc.) adsorb on gold films as $X(CH_2)_nS$ groups (10).

Various transition-metal complexes have been tethered on polymer or inorganic oxide supports using a ligand that coordinates to the transition-metal complex through a donor ligand at one end and to the support through a surfacereactive group at the other end (11). Some of these tethered complexes have been used as catalysts (2). In our previous studies, we formed catalysts by tethering complexes on silica that also contained a supported metal, e.g., Pd (12). These tethered complex on a supported metal (TCSM) catalysts are unusually active for the hydrogenation of arene substrates. In the present report, we describe catalysts that are prepared by tethering a Rh complex directly to the surface of a metal (Au). The tethering ligand is attached to the Au through a thiol group and to the Rh complex by a phosphine or pyridine donor group. It was hoped that an unsaturated organic substrate would be activated by coordination to the Rh complex and hydrogen would be activated by Au to give a catalyst that was more active than either the complex or the Au metal separately. Although gold is generally considered to be a poor catalyst, small-particle gold has recently been reported (13) to be active for alkene hydrogenation. Although there are a few examples (14) of metal complexes tethered on gold, none have been used in catalytic hydrogenation reactions.

In this study, the tethering ligands, methyl 2mercaptonicotinate (MMNT) or 2-(diphenylphosphino)ethane-1-thiol (DPET), were adsorbed on gold powder to give the ligand-modified gold powders MMNT-Au and DPET-Au (Scheme 1). These modified gold powders were reacted with $Rh_2Cl_2(CO)_4$ to give Au powders with tethered rhodiumcarbonyl complexes. We also observed that $Rh_2Cl_2(CO)_4$ could be adsorbed directly onto Au powder without a tether. All three of these rhodium-complex – Au-metal materials were characterized by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy and evaluated for their catalytic activities in the hydrogenation of 1-hexene under the mild conditions of 40°C and 1 atm of H₂.

Experimental

Materials

 $Rh_2Cl_2(CO)_4$ and $HAuCl_4 \cdot xH_2O$ (Au, 49%) were purchased from Strem. The 2-(diphenylphosphino)ethane-1-thiol (DPET) (15) and methyl 2-mercaptonicotinate (MMNT) (16) tethers were prepared by the literature methods. Toluene was dried over CaH₂ before use, while THF, ethanol, and olefin substrates were used directly as commercial products without further purification.

The gold powder was prepared by reducing anhyd $AuCl_3$ (17) with $Li[(C_2H_5)_3BH]$ in THF using the following modified literature procedures (18). Hydrogen tetrachloroaurate (HAuCl_4·3H_2O) (2.00 g) was heated under reflux with



SOCl₂ (20 mL) in a 250 mL flask connected to a mineral oil bubbler in order to prevent moisture from contaminating the reaction mixture. Evolution of SO₂ and HCl was observed while the suspension was heated at reflux, and a red precipitate of anhyd gold(III) chloride was visible in the reaction flask. When the evolution of SO2 and HCl ceased, the remaining SOCl₂ was removed by syringe and the red solid was dried in vacuum (1 mm Hg, 1 mm Hg = 133.322 Pa) at 65°C for 4 h. Then THF (100 mL) was added to the reaction flask, and 20 mL (1.0 M) of a THF solution of $Li[B(C_2H_5)_3H]$ was added dropwise with stirring at room temperature. After stirring for 12 h at room temperature, the mixture was filtered and the solid was washed successively with 80 mL aliquots of THF, methanol, THF, pentane, and water, and then dried under vacuum (0.02 mm Hg) at 80°C. The resulting Au powder was cleaned with freshly prepared "piranha" solution (20 mL) composed of a 50:50 mixture of concd H_2SO_4 and 30% aq H_2O_2 (caution: carefully add the H_2SO_4 to the H_2O_2) in a 250 mL beaker with slow stirring. Nitrogen was blown over the mixture to reduce gold loss due to foaming. The mixture was stirred for 10 min, filtered on a coarse frit, washed with water $(10 \times 50 \text{ mL})$ and ethanol (2 \times 20 mL), and dried under a nitrogen stream. The Au powder was then baked in an oven at 120°C overnight. Routine BET surface area measurements were performed on a Micromeritics AccuSorb 2100 E instrument. With Kr as the adsorbate gas at 77 K, the surface area of the resulting Au powder was determined to be $0.96 \pm 0.07 \text{ m}^2 \text{ g}^{-1}$. An XPS analysis (on an AEI 200B spectrometer) of the Au powder showed it to be pure Au(0). Neither Au(I) nor other impurities such as lithium and boron were detected.

Infrared spectroscopy

All FT-IR and DRIFT spectra were recorded on a Nicolet 710 spectrophotometer equipped with a TGS detector in the main compartment and a MCT detector in the auxiliary experimental module (AEM). The AEM housed a Harrick diffuse reflectance accessory. All solution IR spectra were recorded using a NaCl cell (0.50 mm thickness) in the main compartment with the instrument set for 4 cm⁻¹ resolution and 128 scans. All DRIFT spectra were recorded with samples in the Harrick microsampling cup using 600 scans and 4 cm⁻¹ resolution. The background spectrum used for the DRIFT spectra was clean gold powder. Spectra were routinely baseline and purge corrected. The abscissa of the spectra were recorded and are reported in absorbance units even though the radiation collected is actually reflectance. Kubelka-Munk transformations of the spectra were not possible because of the low intensities of all bands; the bands were eliminated by the transformation. The pseudo-absorbance units used do appear to obey Beer's law, at least approximately.

Preparation of ligand-modified Au powders

MMNT-Au

The Au powder (300 mg) was mixed with a THF solution (1 mL) of methyl 2-mercaptonicotinate (MMNT) (3 mM) in a test tube and shaken for 2 min on a Genie Vortex mixer. After allowing the mixture to stand overnight at room temperature, the solution was separated by centrifugation and analyzed for the amount of MMNT by measuring the intensity of the ester v(C=O) absorption at 1720 cm⁻¹ and converting it to MMNT concentration using Beer's law. Subtracting this concentration from the original concentration of the MMNT solution gave the amount of MMNT (0.30 µmol) adsorbed on the 300 mg sample of Au powder. Increasing the original concentration of MMNT in the THF solution did not change the amount of MMNT adsorbed on the Au powder. The Au solid was washed with THF (1 mL) and dried in vacuum at room temperature to give the MMNT-modified Au powder (MMNT-Au). The DRIFT spectrum of MMNT-Au shows a carbonyl band at 1728 cm⁻¹. This 8 cm⁻¹ increase from that of free MMNT (1720 cm⁻¹) is similar to that observed in the adsorption of $MeO_2C(CH_2)_nSH$ on a Au film (10*a*, 19).

DPET-Au

The Au powder (300 mg) was mixed with a 1,2dichloroethane (DCE) solution (1mL) of 2-(diphenylphosphino)ethane-1-thiol (DPET) (5 mM). After being shaken for 2 min on a Genie Vortex mixer, the mixture was allowed to stand at room temperature overnight. The solution was separated by centrifugation and analyzed for the amount of DPET by measuring the intensity of the C-H stretching absorption at 3073 cm⁻¹ and converting it to DPET concentration using Beer's law. Subtracting this concentration from the original concentration of the DPET solution gave the amount (0.63 µmol) of DPET adsorbed on the 300 mg sample of Au powder. Increasing the original concentration of DPET in the DCE solution did not change the amount of DPET adsorbed on the Au powder. The Au solid was washed with DCE (1 mL) and dried in vacuum at room temperature to give the modified Au powder, DPET-Au.

Preparation of $Rh_2Cl_2(CO)_4$ -modified Au powder catalysts

$Rh_2Cl_2(CO)_4$ adsorbed on Au powder (Rh–Au)

The Au powder (300 mg) was mixed with a toluene solution (1 mL) of $Rh_2Cl_2(CO)_4$ (0.6 mM), and the mixture was stirred at room temperature overnight under an N_2 atmosphere. The solution was separated by centrifugation and analyzed for the amount of $Rh_2Cl_2(CO)_4$ by measuring the intensity of the v(CO) band at 2088 cm⁻¹ and converting it to $Rh_2Cl_2(CO)_4$ concentration using Beer's law. Subtracting this concentration from the original concentration of the $Rh_2Cl_2(CO)_4$ solution gave the amount of $Rh_2Cl_2(CO)_4$ (0.72 µmol) adsorbed on the 300 mg sample of Au powder. The gold powder was washed with toluene (4 × 1 mL) and dried at room temperature under vacuum to give the catalyst Rh–Au. IR (DRIFT) (cm⁻¹): 2105 (s) (CO), 2045 (s) (CO) (Fig. 1).

Fig. 1. DRIFT spectrum of Rh-Au.



$Rh_2Cl_2(CO)_4$ tethered on MMNT-Au (Rh–MMNT-Au)

A mixture of MMNT-Au (300 mg) and a toluene solution (1 mL) of $Rh_2(CO)_4Cl_2$ of the desired concentration was stirred at room temperature overnight under an N_2 atmosphere. The mixture was centrifuged for 5 min to separate the toluene solution. The separated toluene solution was analyzed by the same IR method that was used in the preparation of the Rh–Au catalyst to determine the amount of $Rh_2Cl_2(CO)_4$ adsorbed on the 300 mg of MMNT-Au powder. The Au solid was washed (4 × 1 mL) with toluene and dried in vacuum at room temperature to give the tethered $Rh_2Cl_2(CO)_4$, and the DRIFT spectra of the Rh–MMNT-Au catalysts prepared by using different concentrations of $Rh_2Cl_2(CO)_4$ solutions are shown in Table 1 and Fig. 2.

*Rh*₂*Cl*₂(*CO*)₄ tethered on DPET-Au (*Rh*–DPET-Au)

Rh–DPET-Au was prepared by the same procedure as that used for the preparation of Rh–MMNT-Au using DPET-Au instead of MMNT-Au. The mol of tethered $Rh_2Cl_2(CO)_4$, and DRIFT spectra of the Rh–DPET-Au catalysts prepared by using different concentrations of $Rh_2Cl_2(CO)_4$ solutions are shown in Table 2 and Fig. 3.

Hydrogenation reactions

The hydrogenation reactions were carried out in a 50 mL three-necked jacketed glass-vessel closed with a self-sealing silicon rubber cap and connected to a vacuum–hydrogen line and a constant pressure (1 atm) gas buret. The temperature of the ethylene glycol circulating through the jacket was maintained at 40.0°C by a constant temperature bath. After the catalyst was added and the atmosphere in the vessel was replaced with hydrogen, solvent was added and the mixture was stirred for about 5 min. Then, the substrate was added and the hydrogen volume uptake was followed by the constant-pressure gas buret. The products were analyzed by gas chromatography on a Varian 3400 GC using a 25 m HP-1 capillary column with a FID detector. When the catalyst was used in several successive 1-hexene hydrogenations, the reaction mixture after the first cycle was filtered, and the solid

Entry	Concentration of $Rh_2Cl_2(CO)_4$ before adsorption (mM)	Rh:MMNT mol ratio ^a	Rh adsorbed (µmol) ^b	MMNT:Rh ^c		
a	1.00	9	0.56	0.53		
b	0.60	4	0.56	0.53		
с	0.30	2	0.42	0.71		
d	0.15	1	0.30	1.0		
е	0.075	0.5	0.15	2.0		

Table 1. Adsorption of $Rh_2Cl_2(CO)_4$ from a 1 mL toluene solution on 300 mg of MMNT-Au powder.

^aMol ratio of rhodium in the initial toluene solution to the MMNT ligand adsorbed on 300 mg of MMNT-Au.

^bOn 300 mg of MMNT-Au.

^cRatio on Rh–MMNT-Au.

Fig. 2. DRIFT spectra of the Rh–MMNT-Au samples containing various amounts of rhodium (μ mol) per 300 mg catalyst: (*a*) 0.56; (*b*) 0.56; (*c*) 0.42; (*d*) 0.30; (*e*) 0.15.



catalyst was washed with ethanol, dried under vacuum, and used for the hydrogenation of the second batch of 1-hexene by following the same procedure as that used in the first cycle. After the second cycle, the catalyst was treated as after the first cycle; the isolated catalyst was then used for the third cycle.

Results and discussion

IR characterization of catalysts consisting of $Rh_2Cl_2(CO)_4$ adsorbed or tethered on Au powder

Rh–Au

After stirring a mixture of $Rh_2Cl_2(CO)_4$ and Au powder in toluene at room temperature overnight, IR analyses of both the solution and the Au solid showed that rhodium-carbonyl species were present on the Au powder surface. A DRIFT spectrum (Fig. 1) of the resulting Au powder (Rh–Au) shows two v(CO) bands at 2105 (s) and 2045 (s) cm⁻¹. The DRIFT spectrum of Rh–Au remained the same after it was washed with toluene several times, which indicates that the rhodiumcarbonyl species is strongly adsorbed on the Au surface. Although the v(CO) bands of Rh–Au are similar to those of Rh₂Cl₂(CO)₄ (2115 (w), 2095 (s), and 2045 (s) cm⁻¹ in Nujol[™] mull (20)), they are also similar to those of Rh^I(CO)₂ (approximately 2095 (s) and 2032 (s) cm⁻¹) on SiO₂ or Al₂O₃ (21). Thus, the Rh carbonyl group on Rh–Au appears to be some type of Rh^I(CO)₂ species, perhaps associated with Cl[−] ligands in some way. The broadness of the 2045 cm⁻¹ absorption suggests that other species, perhaps monocarbonyl Rh^I(CO) species, are also present. It is unlikely that any of these species is associated with CO adsorbed on Au as CO does not adsorb on pure Au powder under these conditions.

Rh-MMNT-Au

The tethered Rh₂Cl₂(CO)₄ catalyst Rh-MMNT-Au was obtained by stirring a mixture of Rh₂Cl₂(CO)₄ and MMNT-Au in toluene at room temperature overnight. Table 1 gives the number of mol of rhodium anchored on 300 mg of MMNT-Au when 1 mL toluene solutions of $Rh_2Cl_2(CO)_4$ in concentrations ranging from 0.075 to 1.0 mM were used. The MMNT:Rh ratio on the Au surface ranges from 0.53 to 2.0. In Table 1, it is evident that the number of mol of rhodium anchored on 300 mg of MMNT-Au increases as the initial concentration of $Rh_2Cl_2(CO)_4$ in the toluene solution increases. When the initial concentration of Rh₂Cl₂(CO)₄ in the toluene solution reaches 0.60 mM (Table 1, entry b), the amount of Rh anchored on 300 mg of MMNT-Au is 0.56 µmol and does not increase further when the initial concentration of $Rh_2Cl_2(CO)_4$ in the toluene solution is increased to 1.0 mM. To gain some insight into the structure of the rhodium species, DRIFT spectra (Fig. 2) were recorded on the five Rh-MMNT-Au samples. When the amount of Rh on the MMNT-Au is relatively low (Table 1, entries d and e), the DRIFT spectra (Fig. 2d and e) show one relatively sharp v(CO) band at 2120 (s) cm⁻¹ and one broad band in the region $2060-2000 \text{ cm}^{-1}$; these absorptions are somewhat similar to those of the Rh–Au catalyst (2105 (s) and 2045 (s) cm^{-1}). Although this suggests that the structure of the major rhodium-carbonyl species formed on these two Rh-MMNT-Au samples might be similar to that on Rh–Au, the two v(CO)bands at 2120 (s) and 2060-2000 (vs, br) could also be assigned to the square planar [(*cis*-Rh(MMNT)₂(CO)₂]⁺Cl⁻; the related cis-Rh(py)₂(CO)₂⁺ complex is known to have v(CO) bands at 2095 (vs) and 2020 (vs) cm⁻¹ in CHCl₃ solution (22a). In pyridine solution under a CO atmosphere, cis- $Rh(py)_2(CO)_2^+$ has bands at 2100 and 2038 cm⁻¹ (22b). Still another possible assignment for the species with bands at

Entry	Concentration of $Rh_2Cl_2(CO)_4$ before adsorption (mM)	Rh:DPET mol ratio ^a	Rh adsorbed (μmol) ^b	DPET:Rh ^c
a	3.00	9	0.52	1.2
b	1.00	3	0.48	1.3
с	0.30	1	0.45	1.4
d	0.15	0.5	0.28	2.3

Table 2. Adsorption of $Rh_2Cl_2(CO)_4$ from a 1 mL toluene solution on 300 mg of DPET-Au powder.

^aMol ratio of rhodium in the initial toluene solution to the DPET ligand adsorbed on 300 mg of DPET-Au.

^bOn 300 mg of DPET-Au.

^cRatio on Rh-DPET-Au.

2120 (s) and 2060–2000 (vs, br) cm⁻¹ is Rh(MMNT)(CO)₂Cl; this assignment is based on the v(CO) spectrum of Rh(py)(CO)₂Cl which has bands at 2090 (s) and 2020 (s) cm⁻¹ in CHCl₃ solution (23). In fact, there may be an equilibrium (eq. [1]) between [Rh(MMNT)₂(CO)₂]⁺Cl⁻ and Rh(MMNT)(CO)₂Cl as the MMNT:Rh ratio on the surface decreases from 2.0 to 1.0. This equilibrium may account for the change in band shapes between spectra in Fig. 2*d* and *e*. The shoulder on the low-energy side of the 2060–2000 cm⁻¹ absorption in Rh–MMNT-Au might be attributed to a [Rh(MMNT)₃(CO)]⁺Cl⁻ species based on a 1993 cm⁻¹ band reported for Rh(py)₃(CO)⁺, which was observed in pyridine (22*b*).

[1] $[Rh(MMNT)_2(CO)_2] + Cl^- + 1/2Rh_2Cl_2(CO)_4$

 \neq 2Rh(MMNT)(CO)₂Cl

When the initial mol ratio of Rh-MMNT increases to 2, the Rh–MMNT-Au sample (Table 1, entry d) has v(CO) absorptions at 2120 (s), 2095 (m), and 2030 (s) cm⁻¹. As the initial mol ratio of Rh-MMNT increases further, the relative intensity of the v(CO) band at 2120 cm⁻¹ decreases, but the relative intensity of the v(CO) band at 2095 cm⁻¹ increases. The growth of the 2095 cm^{-1} band (Fig. 2*a*-*c*) is in samples in which the MMNT:Rh ratio is less than 1.0, which means that there is less than one MMNT ligand per Rh. A species with only one MMNT per two Rh atoms is Rh₂Cl₂(CO)₃(MMNT); however, the model complex Rh₂Cl₂(CO)₃(py) for this species is unknown. Another possible species for the 2095 cm⁻¹ band (and probably a companion band at 2030 cm⁻¹) is one in which Rh is bonded to the sulfur atom tethered to the surface. At this point, it is not possible to make an assignment to these new bands. It was also observed that when the Rh-MMNT-Au sample (Table 1, entry d) was stirred in a toluene solution (1 mL) of Rh₂Cl₂(CO)₄ (0.60 mM), an additional 0.24 μ mol of Rh₂Cl₂(CO)₄ was tethered on the Au powder, giving a sample with 0.56 µmol of Rh, which is the same as that of the Rh-MMNT-Au (0.56 µmol) sample used in Table 1, entry b. The DRIFT spectra of these two Rh-MMNT-Au samples are similar as well. Because of the broadness of the v(CO) bands, these assignments are tentative, and it is not possible to exclude the presence of the $Rh^{I}(CO)_{2}$ species resulting from the adsorption of Rh₂Cl₂(CO)₄ directly on the Au.

Fig. 3. DRIFT spectra of the Rh–DPET-Au samples containing various amounts of rhodium (μ mol) per 300 mg catalyst: (*a*) 0.52; (*b*) 0.48; (*c*) 0.45; (*d*) 0.28.



Rh–DPET-Au

The tethered Rh₂Cl₂(CO)₄ catalyst Rh–DPET-Au was prepared by reacting DPET-Au with toluene solutions (1 mL) of Rh₂Cl₂(CO)₄ ranging in concentration from 3.0 to 0.15 mM to give Au powders (Rh-DPET-Au) containing different amounts of tethered Rh₂Cl₂(CO)₄. The data in Table 2 show that the amount of rhodium anchored on 300 mg of DPET-Au increases with an increase in the amount of $Rh_2Cl_2(CO)_4$ in the initial toluene solution; the DPET:Rh ratio on the Au surface increases from 1.2 to 2.3 in the samples. Figure 3 shows that the DRIFT spectra of the four Rh-DPET-Au samples (Table 2) change as the DPET:Rh ratio increases. All of the samples exhibit one relatively sharp v(CO) band at about 2070 cm⁻¹ and one broad v(CO) band in the region 2025–1975 cm⁻¹, and as expected, the intensities of the bands increase as the loading of Rh₂Cl₂(CO)₄ increases. The reaction of Rh₂Cl₂(CO)₄ with PPh₃ in solution is known (24) to give a complicated distribution of various mononuclear $[RhCl(CO)_{3-n}(PPh_3)_n]$ and dinuclear $[Rh_2(\mu-Cl)_2(CO)_{4-m}]$ $(PPh_3)_m$] complexes depending on the ratio of reactants. The complex cis-Rh(PPh₃)(CO)₂Cl is assigned to the two v(CO) absorptions at 2090 (s) and 2005 (s) cm^{-1} , which are in a

Scheme 2.



similar position (2070 and 2025–1975 cm⁻¹) to those (Fig. 3a-c) of the samples in which the DPET:Rh ratio is near unity (1.2–1.4). In the spectrum (Fig. 3d), in which the DPET:Rh ratio is higher (2.3), there is evidence of another band at lower energy, which is similar in position to that reported for *trans*-Rh(PPh₃)₂(CO)Cl (1959 cm⁻¹) (24). Thus, the spectra in Fig. 3 are consistent with *cis*-Rh(DPET)(CO)₂Cl (Scheme 2*a*) as the predominant species at high Rh₂Cl₂(CO)₄ loadings where the DPET:Rh ratio is 1.2–1.4, whereas *trans*-Rh(DPET)₂(CO)Cl (Scheme 2*b*) becomes a contributing species when the DPET:Rh ratio is higher (24). It should be noted that none of the four Rh–DPET-Au samples exhibit v(CO) bands that are characteristic of Rh¹(CO)₂ resulting from the adsorption of Rh₂Cl₂(CO)₄ directly on Au.

Decarbonylation of $Rh_2Cl_2(CO)_4$ adsorbed and tethered on Au powder

The decarbonylation of the Rh-Au and Rh-DPET-Au catalysts was examined by heating under vacuum. Figure 4 shows changes in the v(CO) bands for the Rh–Au catalyst as a function of treatment under vacuum (0.1 mm Hg) and at different temperatures (no absorptions in the 1700–1900 cm⁻¹ range were observed in the DRIFT spectra of any of the heat-treated samples). After treatment at 50-60°C under vacuum for 1.5 h, the v(CO) band at 2105 cm⁻¹ disappeared but the band at 2045 cm⁻¹ remained, although its intensity decreased (Fig. 4b); this suggests that the original $Rh^{I}(CO)_{2}$ species has been lost and small amounts of perhaps a monocarbonyl Rh^I(CO) species remain. After further treatment at 70–80°C for 1.5 h, the v(CO) band at 2045 cm⁻¹ shifted to about 2025 cm^{-1} and broadened (Fig. 4c). After this sample was further treated at 100-110°C for 1.5 h, only a weak, broad band at 2005 cm⁻¹ remained (Fig. 4d). However, when this final sample was stirred in toluene under a CO atmosphere at room temperature overnight, the DRIFT spectrum (Fig. 4e) of the resulting sample was similar to that of the original Rh–Au catalyst, although the v(CO) bands are at slightly lower values, which suggests the formation of a $Rh^{I}(CO)_{2}$ species that is not identical to the original $Rh^{I}(CO)_{2}$ species.

After a sample of Rh–DPET-Au containing 0.45 µmol Rh per 300 mg of DPET-Au was heated at 60°C under vacuum (0.1 mm Hg) for 1.5 h, the DRIFT spectrum showed only three weak v(CO) bands at 2105 (sh), 2076 (s), and 2007 (s, br) cm⁻¹ (Fig. 5*b*). When the heat-treated sample was stirred in toluene under a CO atmosphere at room temperature overnight, the sample exhibited v(CO) bands at 2105 (sh), 2076 (s), and 2007 (s, br) cm⁻¹. The absorptions at 2076 (s) and 2007 (vs, br) indicate that at least some of the original Rh–DPET-Au (2076 (s) and 2008 (s) cm⁻¹) has been regenerated. The v(CO) band at 2105 (sh) corresponds to a Rh¹(CO)₂ species with v(CO) bands at 2105 and 2045 cm⁻¹ (the band at

Fig. 4. DRIFT spectra of Rh–Au as a function of treatment under vacuum (0.1 mm Hg) at different temperatures: (*a*) original; (*b*) 50–60°C for 1.5 h; (*c*) 70–80°C for 1.5 h; (*d*) 100–110°C for 1.5 h; (*e*) after stirring sample (*d*) in toluene under CO (1 atm) at room temperature overnight.



Fig. 5. DRIFT spectra of Rh–DPET-Au with heat and CO treatment: (*a*) original; (*b*) heating at $50-60^{\circ}$ C under vacuum for 1.5 h; (*c*) stirring sample (*b*) in toluene at room temperature overnight under CO (1 atm).



2045 cm⁻¹ would overlap with that of cis-RhCl(CO)₂(DPET) (Scheme 2). Thus, it appears that during the heat treatment, some of the rhodium is deposited on the Au surface and is carbonylated to Rh^I(CO)₂ under CO.

Hydrogenation of 1-hexene with catalysts consisting of $Rh_2Cl_2(CO)_4$ adsorbed and tethered on Au powder

The Rh–Au, Rh–MMNT-Au, and Rh–DPET-Au materials were used to catalyze the hydrogenation of 1-hexene under the conditions of 40°C and 1 atm of H₂. Table 3 gives hydrogenation activities for the homogeneous $Rh_2Cl_2(CO)_4$ and

0

0

	Rh (µmol)	Reaction time (h)	Conversion (%) ^b	Max TOF ^c	TO^d	Yields of products $(\%)^e$		
Catalyst						Hexane	<i>trans</i> -2- Hexene	<i>cis</i> -2- Hexene
Au		7.5	9.2		_	0.7	5.9	2.6
Rh–Au ^f	0.12	2	100	800	29 600	100	0	0
Rh-DPET-Aug	0.08	6	89.7	116	14 500	49	24	16.7
Rh-MMNT-Au ^h	0.08	6	56.3	23.2	6 900	23.3	17.4	15.6
$Rh_2Cl_2(CO)_4$	10	5	0	0	0	0	0	0

0

0

Table 3. Hydrogenation of 1-hexene catalyzed by Rh₂Cl₂(CO)₄ adsorbed and tethered on gold powder.^a

"Reaction conditions: catalyst (50-55 mg), 1-hexene (0.5 mL), ethanol (5 mL), 40°C, 1 atm of H₂.

6

^bConversion of 1-hexene determined by GC at the indicated reaction time.

^cMaximum TOF defined as mol of H₂ uptake per mol rhodium per min.

10

^dTurnover (mol of H₂ uptake per mol Rh) at the indicated reaction time.

eYields of products determined by GC.

 $Rh_2Cl_2(CO)_4 + PPh_3$ (1:1)

^f0.72 µmol Rh per 300 mg catalyst.

^g0.48 µmol Rh per 300 mg catalyst.

^h0.42 µmol Rh per 300 mg catalyst.

Table 4. Hydrogenation of 1-hexene using Rh–MMNT-Au catalysts with different amounts of rhodium.^a

Rh on 300 mg of		
Rh–MMNT-Au (µmol)	Max TOF^b	TO^c
0.15	48.0	10 800(5)
0.30	23.2	6 900(6)
0.42	16.0	3 280(5)
0.56	7.0	1 740(5)

^{*a*}Reaction conditions are the same as those in Table 3. ^{*b*}TOF defined as mol of H_2 uptake per mol Rh per min. ^{*c*}TO (mol of H_2 uptake per mol rhodium) at the indicated reaction time (h) shown in parentheses.

Rh₂Cl₂(CO)₄-PPh₃ (1:1) catalysts, Au powder, Rh–Au, Rh– DPET-Au (0.48 µmol Rh per 300 mg of DPET-Au), and Rh-MMNT-Au (0.42 µmol Rh per 300 mg of MMNT-Au). From the data in Table 3, it can be seen that the homogeneous rhodium complex catalysts Rh₂Cl₂(CO)₄ and Rh₂Cl₂(CO)₄-PPh₃ are inactive for 1-hexene hydrogenation under these mild conditions. The Au powder exhibits a very low activity for the hydrogenation. However, Rh-Au, Rh-MMNT-Au, and Rh-DPET-Au are all active for the hydrogenation of 1hexene under these reaction conditions. Their activities decrease in the following order: Rh-Au > Rh-DPET-Au > Rh-MMNT-Au. The maximum turnover frequency (TOF) and turnover (TO) values for the Rh-Au catalyst are 800 mol H₂ per mol Rh per min and 29600 mol H₂ per mol Rh in 2 h. To the best of our knowledge, this activity is greater than that of any homogeneous or immobilized rhodium complex catalyst for the hydrogenation of 1-hexene reported in the literature (11f, 25-27). For the Rh-DPET-Au and Rh-MMNT-Au catalysts, substantial amounts of isomerization to the 2-hexenes also occur.

Table 4 gives the results of hydrogenation of 1-hexene over Rh–MMNT-Au catalysts with different amounts of rhodium, prepared as described in Table 1. It can be seen that the activities (per mol of Rh) of the Rh–MMNT-Au catalysts decrease as the amount of rhodium on the catalyst increases. This decrease may be due to changes in the catalyst precursor complexes present on the surface at different Rh load-

Table 5. Durability of the Rh–Au and Rh–DPET-Au catalysts in the hydrogenation of 1-hexene.^a

0

Catalyst	Cycle	Max TOF^b	TO^b
Rh–Au	1st	800	29 600(2)
	2nd	528	29 500(2.5)
	3rd	350	28 500(3)
Rh–DPET-Au	1st	116	18 400(6)
	2nd	35	9 640(6)

^aReaction conditions are the same as those in Table 3.

0

^bFootnotes are the same as those in Table 4.

ings. Table 5 shows the durability of the Rh–Au and Rh– DPET-Au catalysts during repeated use in the hydrogenation of 1-hexene. The activities of both catalysts in the second cycle are lower than in the first cycle. The DRIFT spectra of the used Rh–Au and Rh–DPET-Au catalysts, which were isolated from the reaction mixtures after Rh–Au was used for three cycles and Rh–DPET-Au was used for two cycles, show no v(CO) absorptions. Even after these two used catalysts were stirred in toluene under CO (1 atm) overnight, no v(CO) bands were observed in the DRIFT spectra of the samples. Thus, the nature of the Rh species on the Au has changed dramatically during the hydrogenation. It seems unlikely that all of the rhodium has leached from the surface since the catalysts still have appreciable activity after two or three runs even though they exhibit no v(CO) absorptions.

Conclusions

Although the original goal of this investigation was to probe the hydrogenation activities of catalysts that consist of metal complexes tethered on a gold surface, we find that the most active catalyst is Rh–Au in which $Rh_2Cl_2(CO)_4$ is simply adsorbed on gold. This catalyst is far more active than Au metal or $Rh_2Cl_2(CO)_4$ separately. While the initial rhodium species on the Au appears to be some type of $Rh^1(CO)_2$ unit, it loses CO under 1-hexene hydrogenation conditions (40°C, 1 atm H₂). Thus, the active catalyst is a noncarbonyl Rh species, which also does not adsorb CO. Although the active form of the Rh is not known, it is possibly small Rh metal aggregates. The formation of this active Rh species is

apparently facilitated in some manner by the Au. This is supported by the observation that Rh-Au and Rh-DPET-Au undergo decarbonylation even at 55°C under vacuum (0.1 mm Hg), as described above. In contrast, Bhaduri and Khwaja (26c) reported that the catalyst prepared by the reaction of a phosphinated polystyrene with $Rh_2Cl_2(CO)_4$ does not undergo decarbonylation even when heated at 120°C under vacuum (1 \times 10⁻³ mm Hg) for 24 h. It has also been reported that the intensities and positions of the v(CO) bands for a material prepared by adsorbing $Rh_2Cl_2(CO)_4$ from toluene solution onto Al_2O_3 do not change when it is heated at 80°C under 1 atm of H₂ for 1 h (21). This suggests that the Au powder facilitates the decarbonylation of the rhodium carbonyl complex adsorbed or tethered on it. Another possible role played by the Au powder support is the creation of an unusually active form of Rh for 1-hexene hydrogenation.

While less active, the tethered Rh complex catalysts, Rh– DPET-Au and Rh–MMNT-Au, also catalyze the hydrogenation of 1-hexene. Under the hydrogenation conditions, the Rh complexes that are present in the unused catalysts lose their CO ligands to generate a noncarbonyl form of Rh, perhaps the same as that formed from Rh–Au, which is the catalytically active species. The activities of the Rh–Au and Rh–DPET-Au catalysts decrease upon repeated use. This decrease may be due to migration of the Rh(0) into the Au to form an inactive alloy.

These studies demonstrate that it is possible to form active hydrogenation catalysts by adsorbing Rh complexes on Au metal. Although Au is too expensive to be used as a catalyst support for most studies, the results do suggest that the adsorption of metal complexes on less expensive metal supports may lead to unusually active hydrogenation catalysts.

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