

Articles

Surface Organometallic Chemistry on Oxides: Reaction of CO with Bis(allyl)rhodium Grafted onto Silica, Titania, and Alumina

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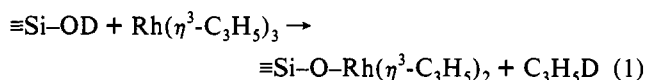
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Tris(allyl)rhodium(III) reacts with the hydroxyl-terminated surfaces of silica, titania, and alumina to form a surface bis(allyl)rhodium(III) fragment. In the presence of CO, this supported organometallic fragment undergoes a series of reactions which model elementary steps of heterogeneous C–C and C–O bond formation. On surfaces with low proton content (silica-400, alumina, titania), 1,5-hexadiene is produced quantitatively by reductive coupling of two allyl ligands, with simultaneous formation of surface-bound dicarbonylrhodium(I). In the presence of a high concentration of surface protons (silica-200), there are two reaction pathways: (i) formation of propene by reaction of an allyl ligand with a surface proton and (ii) insertion of CO into the metal–carbon bond to give the acyl complex $\text{CH}_2=\text{CHCH}_2\text{C}(\text{O})\text{Rh}^{\text{III}}$, detected by IR. The acyl ligand may undergo reductive elimination with an allyl ligand, giving the minor product 1,6-heptadien-4-one, or with a siloxy ligand, with transfer of 3-butenolate to the silica support (extracted as methyl-3 butenoate). The dicarbonylrhodium(I) product is mobile on the surface of silica: dimerization occurs spontaneously. Under H_2 , reduction and aggregation of the dimers leads to small metal particles.

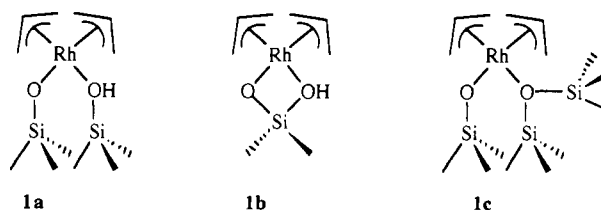
Introduction

Surface organometallic fragments are likely candidates for intermediates in heterogeneous catalysis,^{1,2} where reactivity remains ill-defined by comparison to homogeneous systems. The study of the stoichiometric reactivity of well-defined surface organometallic fragments is designed to elucidate the elementary steps of heterogeneous mechanisms, leading to a better understanding of catalytic reactivity. The mechanisms and selectivity of C–C and C–O bond formation on surfaces is particularly important: supported Rh catalysts are effective at converting syn gas into C_2 -oxygenates,³ while homogeneous Rh hydroformylation catalysts are used for the large-scale conversion of olefins to alcohols, aldehydes, and esters.⁴

As originally discovered by Ward and Schwartz,^{5,6} and subsequently confirmed in other laboratories,^{7,8} $\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3$ reacts with the surface of partially dehydroxylated silica to give a grafted bis(allyl)rhodium(III) complex. The surface reaction, electrophilic cleavage of a rhodium–carbon bond by a surface proton with formation of a rhodium–oxygen bond to the surface, has been demonstrated by isotopic labeling of silanols,⁹ eq 1. It has been proposed on the basis of IR evidence⁸ and theoretical



calculations¹⁰ that the Rh atom is linked to the surface by more than one surface oxygen, *i.e.*, that Rh accepts electron donation from an adjacent silanol or siloxane group, so that the supported complex attains an 18-electron configuration. There are several possible local structures on silica surfaces, however, the primary coordination sphere of Rh (two allyl ligands and two oxygen donor ligands) is the same for all of them:⁸



Similar reactions between $\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3$ and partially dehydroxylated titania^{6,11} and alumina^{8,12} have been studied. Because of the lower surface hydroxyl density on these oxides, structures were proposed for $\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_2(\text{OTi})$, **2**, and $\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_2(\text{OAl})$, **3**, in which the Rh atom achieves an 18-electron configuration by bonding to oxygen atoms of adjacent Ti–O–Ti and Al–O–Al bridges, respectively.⁸

As part of our general study of the stoichiometric reactivity of surface organometallic fragments, we have already examined the reactions between **1–3** and H_2 .^{13,14} In this paper, we report our findings on the reaction of the bis(allyl)rhodium surface

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complexes with CO, in which C–C and C–O bond formation is observed. The transfer of an acyl ligand from Rh to the silica surface by reductive elimination with a siloxy ligand is analogous to the mechanism of carboalkoxylation, in which esters are formed by the combination of acyl and alkoxy ligands.¹⁵ As a homogeneous model for the surface processes, the reaction of $[\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_2\text{Cl}]_2$ with CO was also examined. Similarities between homogeneous and heterogeneous intermediates and products are reported and provide evidence for the “molecular” nature of the surface reactions.

Results

Grafting of $\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3$ onto Oxide Surfaces. The reaction of $\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3$ with partially dehydroxylated oxide surfaces has already been described.⁸ Sublimation of $\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3$ onto a silica pellet, dehydroxylated in vacuum at 200 or 400 °C, leads to formation of $(\equiv\text{SiO})(\equiv\text{SiOX})\text{Rh}^{\text{III}}(\eta^3\text{-C}_3\text{H}_5)_2$, **1** (X is H, Si≡), with evolution of 1 equiv of propene and the appearance in the IR spectrum of bands due to $\nu(\text{C-H})$ at 3048 and 2992 cm^{-1} , $\delta(\text{CH}_2)$ at 1492 and 1462 cm^{-1} , and $\nu(\text{C-C-C})$ at 1391 cm^{-1} , Figure 1. In addition, a small sharp band at 3636 cm^{-1} appears, which has been attributed to $\nu(\text{OH})$ of a very rigid silanol group bonded to the bis(allyl)rhodium fragment in structure **1b**.⁸ The silica-supported complex **1** is deep yellow.

Reaction of $1/\text{SiO}_2(400)$ with CO. Volumetry. When **1** was grafted onto $\text{SiO}_2(400)$,¹⁶ the addition of 0.1 Torr of CO led to the formation of 1 equiv of 1,5-hexadiene per Rh, detected and identified by GC and GC-MS. Very little propene was detected.

IR Spectroscopy. The reaction with CO caused all the IR bands of $1/\text{SiO}_2(400)$ to disappear, *except for the $\nu(\text{OH})$ band at 3636 cm^{-1}* . At the same time, a pair of intense bands characteristic of oxide-bound *gem*-dicarbonylrhodium(I)^{17,18} appeared at 2087 and 2012 cm^{-1} , Figure 2a. The dicarbonylrhodium(I) species, **4**, is relatively unstable. Over 30 min, the bands at 2087 and 2012 cm^{-1} were replaced by three new bands at 2109 (m), 2092 (s), and 2035 (s) cm^{-1} , Figure 2b. The positions and intensities of these three bands suggest the formation of dimeric dicarbonylrhodium(I), **5**. In particular, the high-frequency band is characteristic of nonplanar dicarbonylrhodium(I) dimers, such as $[\text{Rh}(\text{CO})_2\text{X}]_2$, where X is Cl and OH.^{19,20} The $\nu(\text{OH})$ band at 3636 cm^{-1} disappears during dimerization. The dimerization reaction of the dicarbonylrhodium(I) species was observed regardless of the CO pressure.

Isotopic Labelling. The nuclearity of the silica-supported dicarbonylrhodium(I) species **4** (monomer) and **5** (dimer) was verified by exposure of the supported complexes to mixtures of ^{12}CO and ^{13}CO , shown for **4** in Figure 3. The number and positions of the $\nu(\text{CO})$ bands can be predicted for monomeric and dimeric complexes by consideration of the symmetry of the possible isomers (see supplementary material).^{21,22} A comparison between experimental and calculated peak positions is shown in Tables 1 and 2. The peak positions for the dimeric **5** agree with published values.^{7,12}

These results are consistent with a clean stoichiometric reaction on silica₍₄₀₀₎, eq 2. The primary organometallic product is the

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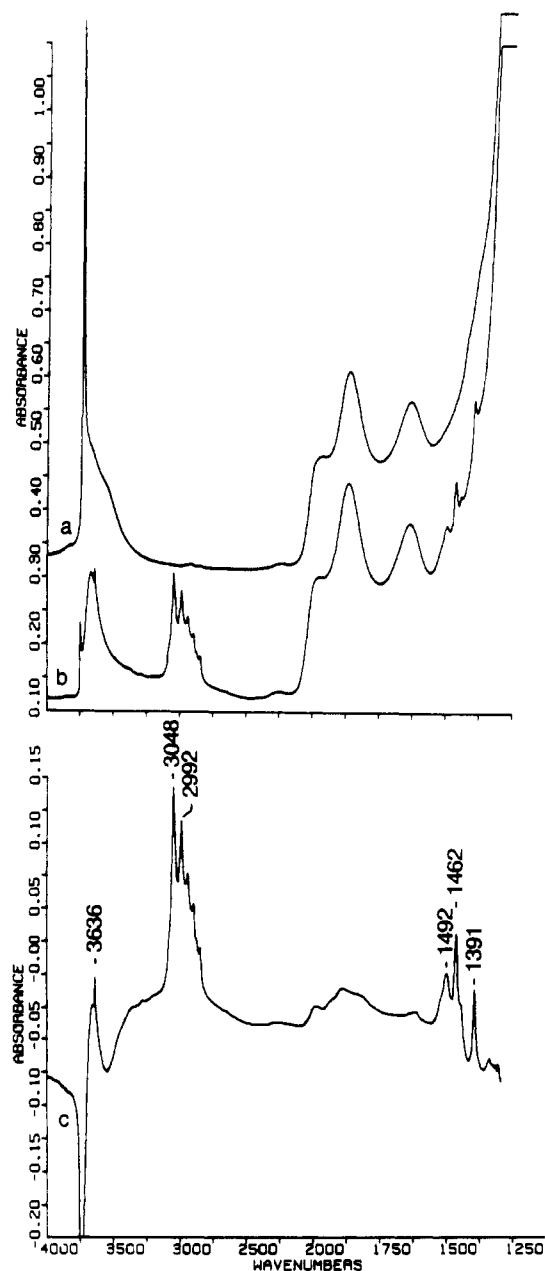
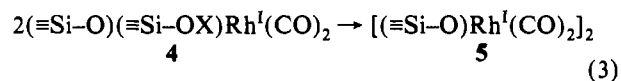
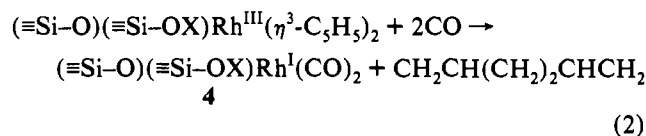


Figure 1. Infrared spectra of $(\equiv\text{SiO})(\equiv\text{SiOX})\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_2$, **1**, where X is H or Si≡: (a) $\text{SiO}_2(200)$, before grafting; (b) after reaction with $\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3$ and desorption of unreacted material; (c) the difference spectrum (b) – (a).

dicarbonylrhodium(I) monomer, **4**, which spontaneously dimerizes on the silica surface, eq 3.



Reaction of $1/\text{SiO}_2(200)$ with CO. Volumetry. When $1/\text{SiO}_2(200)$ was treated with 0.1–10 Torr of CO, propene was the major gas phase product. Traces of allyl alcohol and 1,6-heptadien-4-one were also detected. Volumetric measurements (Table 3) indicate that the amount of hydrocarbon released by the reaction of $1/\text{SiO}_2(200)$ with 10 Torr of CO correspond to *ca* 1.2 equiv of C_3

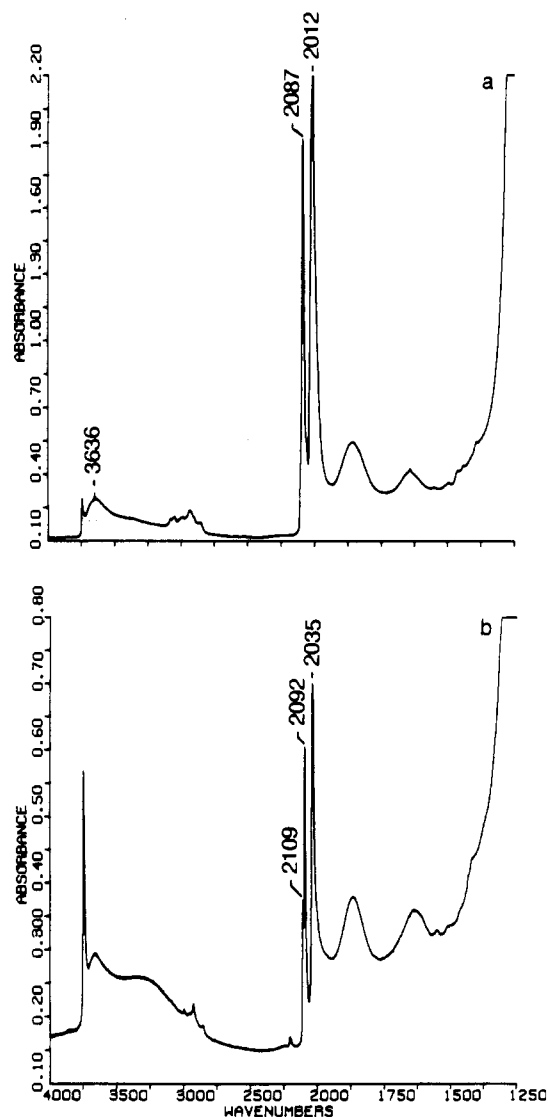


Figure 2. Infrared spectra obtained following the addition of 0.1 Torr of CO to $(\equiv\text{SiO})(\equiv\text{SiOX})\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_2$, **1**/ $\text{SiO}_2(400)$: (a) Spectrum recorded immediately after addition of CO; (b) spectrum recorded after 30 min.

hydrocarbon per Rh, compared to the 2 equiv expected for complete reaction. Therefore, the surface has withheld (retained as chemisorbed species) 0.8 equiv of C_3 per Rh. At the same time, 2.6 equiv of CO per Rh was irreversibly consumed. This value is greater than that expected based on the quantitative formation of **4** and/or **5** (i.e., 2 CO/Rh).

A small quantity of CO_2 was detected in the presence of 10 Torr of CO. The formation of this product is probably not associated with reactions of the allyl ligands (see Discussion).

IR Spectroscopy. On silica-200, the dicarbonylrhodium(I) monomer and dimer species were observed by IR, as described above. However, in contrast to the chemistry on $\text{SiO}_2(400)$, several new bands were observed at 3089, 2929, 1692, 1642, 1553, and 1430 cm^{-1} , Figure 4. The bands at 3089 and 1642 cm^{-1} correspond to olefinic C–H and C=C stretching modes, respectively.²³ The band at 2929 cm^{-1} is assigned to a $\nu_{\text{as}}(\text{CH}_2)$ mode. From these assignments, we infer the presence of a σ -allyl ligand, $-\text{CH}_2\text{-CH}=\text{CH}_2$, at the surface.²⁴ The 1692 cm^{-1} band is attributed to the $\nu(\text{C}=\text{O})$ stretching mode of an acylrhodium(III) complex.^{25–27} It lies on top of a band at 1713 cm^{-1} , which we assign to the $\nu(\text{C}=\text{O})$ mode of a silyl ester (see below). The

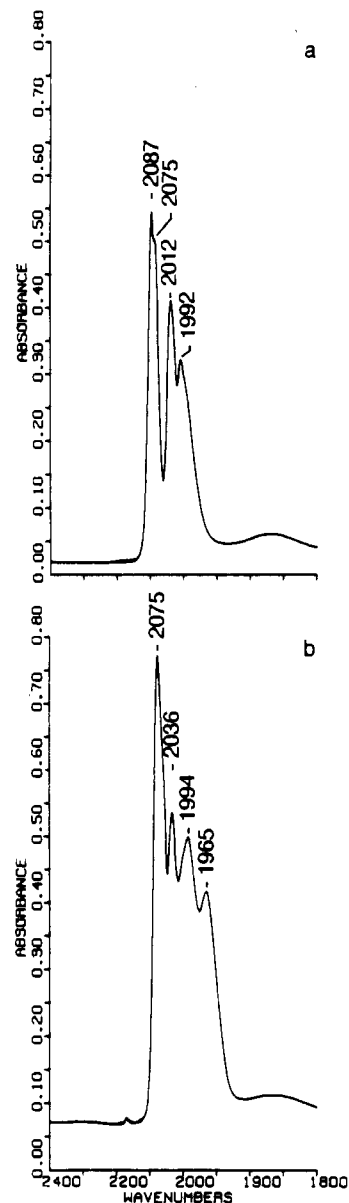


Figure 3. Infrared difference spectra in the $\nu(\text{CO})$ region of monomeric $(\equiv\text{SiO})(\equiv\text{SiOX})\text{Rh}^{\text{I}}(\text{CO})_2$, **4**, in the presence of a $^{13}\text{CO}/^{12}\text{CO}$ mixture (65/35): (a) **4** prepared from the reaction of **1** with ^{12}CO and then exposed to the isotopic mixture; (b) **4** prepared from the reaction of **1** with ^{13}CO and then exposed to the isotopic mixture. The spectrum of $\text{SiO}_2(400)$ was removed by subtraction.

Table 1. IR Peak Positions (cm^{-1}) of $\nu(\text{CO})$ Bands for Monomeric Oxide-Supported Dicarboxylrhodium(I) Complexes in the Presence of an Isotopic Mixture $^{12}\text{CO}/^{13}\text{CO}$

gas composn	$\text{Rh}^{\text{I}}(\text{CO})_2$ on silica		$\text{Rh}^{\text{I}}(\text{CO})_2$ on alumina	
	obsd	calcd ^a	obsd	calcd ^a
$^{12}\text{CO}/^{12}\text{CO}$	2087	2087	2091	2096
	2012	2012	2021	2021
$^{12}\text{CO}/^{13}\text{CO}$	2075	2070	2081	2079
	1992	1983	1992	1995
$^{13}\text{CO}/^{13}\text{CO}$	2036	2041	2046	2049
	1965	1967	1976	1979

^a See supplementary material.

bands at 1553 and 1430 cm^{-1} are assigned to the asymmetric and symmetric vibrations, respectively, of a bidentate carboxylate

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Table 2. IR Peak Positions (cm⁻¹) of $\nu(\text{CO})$ Bands for Silica-Supported Dimeric Dicarboxylrhodium(I) Complexes in the Presence of an Isotopic Mixture ¹²CO/¹³CO

complex	obsd	calcd ^a
Rh ₂ (¹² CO) ₄	2107	2103
	2089	2085
	2036	2030
Rh ₂ (¹² CO) ₃ (¹³ CO)	2076	2098
	2044	2076
	2005	2041
	2005	2006
<i>cis</i> -Rh ₂ (¹² CO) ₂ (¹³ CO) ₂	2089	2086
	2076	2073
		2014
	2005	2001
	2089	2088
<i>trans</i> -Rh ₂ (¹² CO) ₂ (¹³ CO) ₂	2076	2070
		2018
		1999
		2096
		2046
<i>gem</i> -Rh ₂ (¹² CO) ₂ (¹³ CO) ₂	2044	2041
	2044	2041
	1989	1992
Rh ₂ (¹² CO)(¹³ CO) ₃		2081
	2044	2046
		2012
Rh ₂ (¹³ CO) ₄	1989	1990
	2056	2056
	2044	2039
		1985

^a See supplementary material. Values of force constants and coupling constants: $f = 1725$, $f' = 45.7$, $\alpha = 15.2$, $\beta = 0 \text{ N}\cdot\text{m}^{-1}$.

Table 3. Gases Evolved by the Interaction of **1**/SiO₂(200) with 10 Torr of CO^a

evolved gas	quantity/mmol	C ₃ equiv
propene	0.097	0.71
1,5-hexadiene	0.032	0.47
1,6-heptadien-4-one	0.001	
allyl alcohol	trace	
3-butenic acid	not detected	
carbon dioxide	0.032	

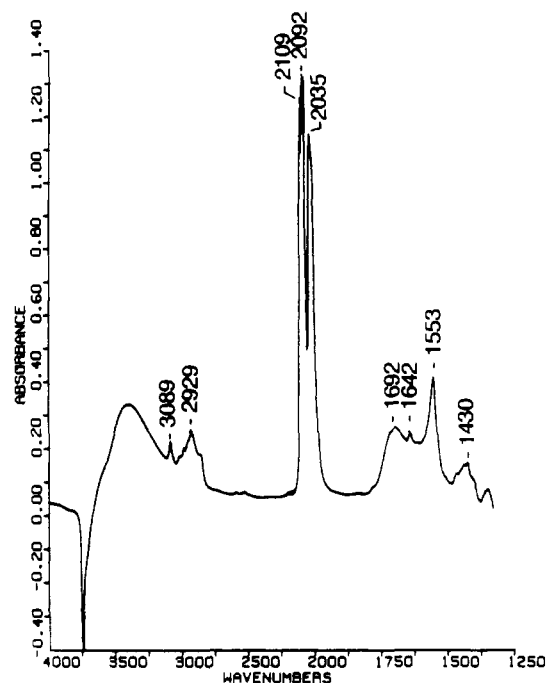
^a 0.137 mmol of Rh(allyl)₃ reacted with 2 g of silica (SHELL200); the Rh content determined by atomic absorption was 0.70% (theoretical 0.63%). A 0.391-mmol amount of CO was introduced. After reaction, 0.035 mmol of CO remained. Therefore the consumption of CO was 2.6 CO/Rh.

group. Peak positions and assignments are summarized in Table 4.

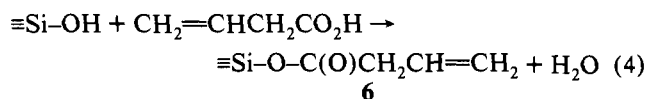
The allyl, acyl, ester, and carboxylate fragments are strongly held on the surface. The intensities of the IR bands associated with these groups were unchanged by prolonged exposure to dynamic vacuum. Note that the formation of acyl, ester, and carboxylate species is consistent with the consumption of excess CO (0.6 per Rh) as determined by volumetry.

Extraction of Surface Ester and Carboxylate Species. The organic fragments bound to the surface were extracted with both (CH₃)₂SO₄ and CH₃I.^{28,29} The extracted product, the methyl ester CH₃OC(O)CH₂CH=CH₂, was identified by chromatography. However, it polymerized readily in the presence of Me₂SO₄ and so decreased in concentration during the course of the analysis. The extraction was repeated following *in situ* hydrogenation of the surface species (see below). The corresponding saturated methyl ester, CH₃OC(O)CH₂CH₂CH₃, was obtained. Neither the unsaturated nor the saturated ester was found in a blank experiment involving **1**.

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**Figure 4.** Infrared difference spectrum obtained after the reaction of ($\equiv\text{SiO}$)($\equiv\text{SiOX}$)Rh($\eta^3\text{-C}_3\text{H}_5$)₂, **1**/SiO₂(200), with 10 Torr of CO for 30 min. The spectrum of SiO₂(200) was removed by subtraction.

Chemisorption of Authentic 3-Butenoic Acid on Silica. Sublimation of 3-butenic acid onto silica-200 results in the partial disappearance of the $\nu(\text{O-H})$ mode at 3748 cm⁻¹ and the appearance of new bands at 3089, 2920, 1725, 1645, 1415, and 1376 cm⁻¹, corresponding to the silyl ester of 3-butenic acid, **6**.



The ester is strongly held on the surface: the IR bands were not diminished by prolonged dynamic vacuum (10⁻⁴ Torr, 16 h). The $\nu(\text{C}=\text{O})$ frequency of the surface-bound ester (1725 cm⁻¹) is lower than that of the free acid (1741 cm⁻¹), probably due to hydrogen-bonding to adjacent silanols. The IR spectrum of the ester **6** is similar to the spectrum of the silyl ester formed by the reaction of **1** with CO ($\nu(\text{CO})$ at 1713 and 1747 on silica-200 and silica-400, respectively). However, there is no evidence for the formation of a bidentate carboxylate of 3-butenic acid obtained by the reaction of **1** with CO, with $\nu(\text{CO}_2)$ at 1553 and 1430 cm⁻¹. (To determine whether the presence of metallic rhodium could influence the coordination mode of 3-butenic acid on silica, the above experiment was repeated on SiO₂(200) in the presence of dispersed metallic rhodium covered with CO. The $\nu(\text{C}=\text{O})$ band of **6** appeared at 1727 cm⁻¹ and remained unchanged for a period of 48 h.)

Reaction of Surface Complexes with H₂. In the presence of 100 Torr of H₂ at room temperature, a large increase in intensity in the $\nu(\text{OH})$ (hydrogen-bonded) region was observed, Figure 5. The $\nu(\text{C-H})$ and $\nu(\text{C=C})$ modes at 3089 and 1642 cm⁻¹, respectively, disappeared, while new bands appeared at 2968 and 2880 cm⁻¹, implying hydrogenation of surface allyl groups to propyl. The small band at 1692 cm⁻¹, attributed to the $\nu(\text{C}=\text{O})$ mode of acylrhodium(III), also disappeared, as did the carboxylate bands at 1553 and 1430 cm⁻¹ (over 48 h). The bands corresponding to alkyl $\nu(\text{C-H})$ and ester $\nu(\text{C}=\text{O})$ vibrations were stable under H₂ and subsequent prolonged dynamic vacuum at room temperature, indicating that these groups are still strongly held on the surface.

During the reaction with H₂ at room temperature, the color of the sample changed from yellow to black. Small metal particles,

Table 4. IR Spectroscopy of Rh Surface Complexes Formed in the Reaction of Rh(allyl)₂/SiO₂ with CO and H₂

surface compd	surface peak posn/cm ⁻¹	vibrational assgnt	model peak posn/cm ⁻¹	model compd
(=SiO)(=SiOX)Rh(CO) ₂ (4)	2087, 2012	$\nu(\text{C}=\text{O})$	2074, 2018	Rh(CO) ₂ aca ^a
(=SiO) ₂ (CO) ₂ RhC(O)CH ₂ CH=CH ₂ (12)	3089 2929 1692 1642	$\nu(\text{C}=\text{H})$ $\nu_{\text{as}}(\text{CH}_2)$ $\nu(\text{C}=\text{O})$ $\nu(\text{C}=\text{C})$		[Rh($\eta^3\text{-C}_3\text{H}_5$)(C(O)C ₃ H ₅)Cl] ₂ ^b
Rh(O ₂ CCH ₂ CH=CH ₂)/SiO ₂	1553 1430	$\nu_{\text{as}}(\text{CO}_2)$ $\nu_s(\text{CO}_2)$	1693 1642 1560	[Rh(CO) ₂ O ₂ CCH ₃] ₂ ³⁰
=Si-O-C(O)CH ₂ CH=CH ₂ (6)	3089 2929 1713 1642	$\nu(\text{C}=\text{H})$ $\nu_{\text{as}}(\text{CH}_2)$ $\nu(\text{C}=\text{O})$ $\nu(\text{C}=\text{C})$	3089 2920 1725 1645	=Si-O-C(O)CH ₂ CH=CH ₂ ^c
[(=SiO)Rh(CO) ₂] ₂ (5)	2109, 2092, 2035	$\nu(\text{C}=\text{O})$	2089, 2076, 2015	[Rh(CO) ₂ Cl] ₂ ¹⁵
Rh ⁰ (CO) _x /SiO ₂	2047 1875	$\nu(\text{C}=\text{O})$ linear $\nu(\text{C}=\text{O})$ bridging		

^a Bonati, F.; Wilkinson, G. *J. Chem. Soc.* **1964**, 3156. ^b This work. Spectrum recorded at -60 °C in CDCl₃. ^c Sample prepared independently by chemisorption of 3-butenic acid on silica.

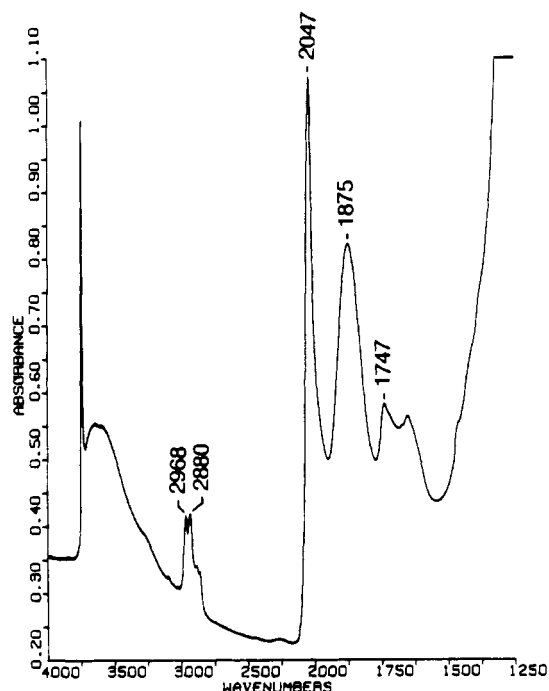


Figure 5. Infrared spectrum obtained after treatment of [(=SiO)Rh⁰(CO)₂]₂, **5**/SiO₂₍₄₀₀₎, with 100 Torr of H₂ at room temperature for 72 h, followed by evacuation for 1 h at ambient temperature.

varying in diameter from 2 to 4 nm, were observed by electron microscopy. Intense, broad bands at 2047 and 1875 cm⁻¹ appeared in the IR spectrum, Figure 5. These frequencies are associated with terminal and bridging carbonyl ligands on Rh crystallites.³⁰⁻³² The $\nu(\text{CO})$ bands were displaced to 2032 and 1857 cm⁻¹ under dynamic vacuum at 25 °C for 48 h.³³

Effect of Rh Coverage. On SiO₂₍₄₀₀₎, when the amount of grafted Rh was small (as judged by a large amount of remaining surface hydroxyl groups), the chemistry had some similarities to that observed on SiO₂₍₂₀₀₎. Both propene and hexadiene were observed in the gas phase. On the surface, formation of ester and carboxylate species was observed. The $\nu(\text{C}=\text{O})$ mode of the silyl ester appeared at 1747 cm⁻¹, compared to 1713 cm⁻¹ on SiO₂₍₂₀₀₎. (Note that the shift $\Delta\nu(\text{CO})$ can be as large as 25 cm⁻¹ depending on the degree of hydrogen-bonding to the carbonyl oxygen.²³) Under H₂, as the hydroxyl content of the surface

increased, this band shifted from 1747 to 1710 cm⁻¹ but shifted back to 1747 cm⁻¹ after vacuum treatment.

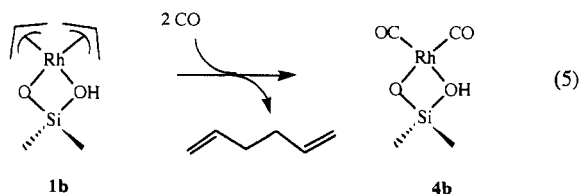
A Model Homogeneous Reaction: Interaction of [Rh($\eta^3\text{-C}_3\text{H}_5$)₂Cl]₂ with CO. The interaction of the model compound [Rh($\eta^3\text{-C}_3\text{H}_5$)₂Cl]₂³⁴ with CO in CDCl₃ solution was followed by IR and ¹H and ¹³C NMR. Upon exposure to 1 atm of CO at -60 °C, a new IR band corresponding to CO coordinated to Rh(III) was observed at 2073 cm⁻¹. By ¹H NMR, the reactant dimer is transformed to [Rh($\eta^3\text{-C}_3\text{H}_5$)₂(CO)Cl] at -60 °C, as described previously.³⁵ When CO was continuously bubbled through the solution at -20 °C, three new peaks appeared in the ¹³C NMR spectrum at 36.0, 101.2, and 131.7 ppm, due to the formation of a σ -allyl ligand.³⁶ Conversion of an allyl ligand from π -bound to σ -bound was also inferred by IR and by the appearance of the $\nu(\text{C}=\text{C})$ mode at 1642 cm⁻¹. Subsequent insertion of CO into the Rh-C bond gave an acylrhodium(III) intermediate with $\nu(\text{C}=\text{O})$ at 1693 cm⁻¹. The final product (at low temperature) was monomeric dicarbonylrhodium(I), with $\nu(\text{CO})$ bands at 2074 and 2018 cm⁻¹. The organic products 1,5-hexadiene and 1,6-heptadien-4-one were identified by GC and GC-MS.

Results on Other Oxides: Titania and Alumina. During the interaction of **2** and **3** with CO, 1,5-hexadiene was released into the gas phase. Propene was detected only in very small quantities (note that the proposed structures for **2** and **3** contain no hydroxyl group, and therefore no available proton, in the coordination sphere of Rh).⁸ On both titania and alumina, a monomeric *gem*-dicarbonylrhodium(I) species was observed, with $\nu(\text{CO})$ modes at 2095 and 2018 cm⁻¹ (titania, **7**) and 2091 and 2021 cm⁻¹ (alumina, **8**), respectively.

The number and position of these bands did not change with the length of exposure to CO. The reaction of **2** with a mixture of ¹²CO/¹³CO was studied, with results shown in Table 1. Comparison to the calculated^{21,22} positions of the $\nu(\text{CO})$ bands confirms the monomeric structure of **7**.

Discussion

On SiO₂₍₄₀₀₎ at high Rh coverage, coordination of CO to **1** is accompanied by a shift of the coordinated allyl ligands from π -bound to σ -bound, followed by reductive elimination of 1,5-hexadiene, eq 5. In the case of species **1b**, reaction with CO leaves the rigid silanol ligand coordinated to **4b**, and the band at 3636 cm⁻¹ is still present after elimination of the allyl ligands.



With higher surface hydroxyl content (using SiO₂₍₂₀₀₎) or a low Rh coverage on SiO₂₍₄₀₀₎, other reaction pathways were also

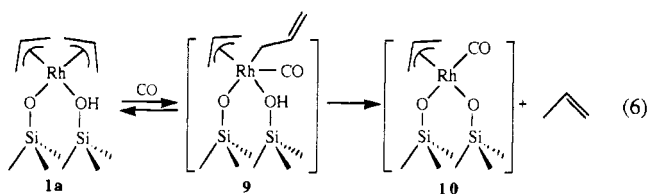
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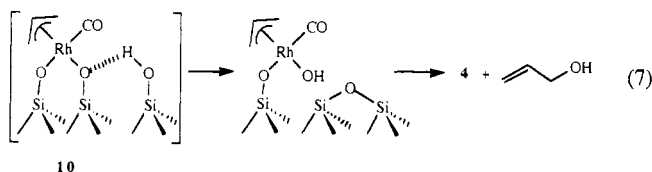
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observed. In this case, propene is the major product, formed by reaction of an allyl ligand with a surface proton, eq 6. This



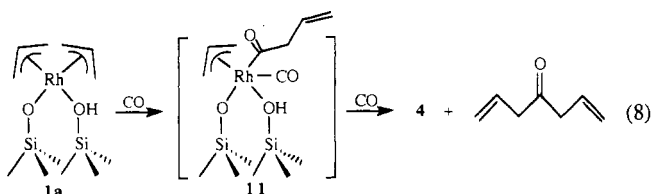
surface proton probably originates in a silanol ligand in or near the coordination sphere of Rh. The role of the silanol ligand is analogous to that of organic alcohols in homogeneous reactions. For example, the reaction of $(\text{PR}_3)_3\text{RhR}$ with $\text{R}'\text{OH}$ in toluene results in the formation of RH and $(\text{PR}_3)_3\text{RhOR}'$.³⁷

Reductive elimination of the remaining allyl ligand with a hydroxyl group gives allyl alcohol, detected in trace amounts, eq 7. The hydroxyl group in the coordination sphere of Rh may be



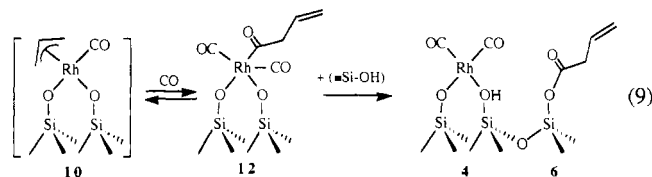
created by reaction with surface silanols (with simultaneous formation of a siloxane bridge). The reductive elimination of allyl alcohol is similar to the formation of allyl chloride from $\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_2\text{Cl}_2$, which is enhanced when L is a π -acidic ligand such as CO .³⁸

CO Insertion. When CO insertion precedes elimination of propene, the (allyl)(acyl)rhodium complex **11** is formed. Traces of 1,6-heptadien-4-one are produced by reductive elimination from **11**, eq 8. Homogeneous (alkyl)(acyl) Rh^{III} complexes such



as $[\text{RhR}(\text{C}(\text{O})\text{R}')(\text{CO})(\text{Cl})\text{L}_2]$ are unstable and rapidly eliminate ketone.³⁹ CO insertion into $\text{Rh}-\text{C}$ bonds has been proposed on metallic Rh surfaces under CO/H_2 ⁴⁰⁻⁴² and for silica-supported $[\text{Rh}(\text{C}_5\text{Me}_5)(\text{CH}_3)]_2(\mu\text{-CH}_2)_2$.⁴³ Reductive elimination of 1,6-heptadien-4-one was observed in the reaction of molecular bis(allyl)nickel complexes with CO .⁴⁴

Insertion of CO may also occur after elimination of propene, eq 9. In the absence of an alkyl ligand, the acylrhodium(III)



complex **12** is stable enough to be observed. A small band at 1692 cm^{-1} is attributed to the acyl $\nu(\text{CO})$ of **12**, by comparison to spectra of other acylrhodium(III) complexes, e.g., 1708 cm^{-1} for the molecular complex $[\text{Rh}(\text{COMe})\text{Cl}_2(\text{PPh}_3)_2]_2$ ²⁵ and 1710 cm^{-1} for silica-supported (propanoyl)rhodium(III).⁴³ (Note that acyl ligands coordinated to rhodium(I) have significantly lower $\nu(\text{C}=\text{O})$ frequencies, $1650\text{--}1670\text{ cm}^{-1}$.)²⁵⁻²⁷ Since **12** is a minor species, the $\nu(\text{CO})$ bands for its carbonyl ligands cannot be distinguished from those of the major products **4** and **5**. The acylrhodium(III) complex is unstable under H_2 .

Reductive elimination of the acyl ligand with a siloxy ligand coordinated to Rh occurs to give the silyl ester of 3-butenolate, eq 9. Evidence for the silyl ester **6** is the appearance of a peak at 1713 cm^{-1} (on $\text{SiO}_2(200)$) or 1747 (on $\text{SiO}_2(400)$), which is stable under H_2 and under dynamic vacuum. The shift to higher frequency on the more dehydroxylated silica is consistent with less H-bonding of the acyl carbonyl to adjacent silanols.⁴⁵ In homogeneous chemistry, reductive elimination of acyl chloride from $\text{Rh}(\text{R})(\text{PPh}_3)_2\text{Cl}_2$ (R is ethyl, vinyl,⁴⁶ or allyl⁴⁷) was observed in the presence of CO .

The formation of **6** seems to be the first well-documented example of the transfer of an acyl group to a surface oxygen of an oxide support. This elementary step may be important in the formation of oxygenates during CO/H_2 conversion on metal surfaces. In that reaction, a band at 1749 cm^{-1} observed on a Rh/SiO_2 catalyst was assigned to the formation of silyl acetate $\equiv\text{Si}-\text{O}-\text{C}(\text{O})\text{CH}_3$.

Carboxylate Formation. The bands at 1553 and 1430 cm^{-1} , corresponding to the asymmetric and symmetric stretching frequencies of a bidentate carboxylate group, cannot be attributed to the silyl ester **6**. The blank experiment (chemisorption of 3-butenic acid on silica) showed that carboxylic acids form only monodentate esters on silica. We propose therefore that the bidentate carboxylate is coordinated to rhodium. Bidentate acetate species ($\nu(\text{CO}_2)$ 1564 , 1442 cm^{-1}) were also observed during CO/H_2 conversion over Rh/SiO_2 catalysts.⁴⁵ Oxygen incorporation from silica into surface-bound rhodium acetyl species was invoked to explain the distribution of ^{18}O labels.⁴² A bidentate (3-butenato)rhodium species could be formed by nucleophilic attack of a hydroxyl ligand derived from silica (eq 7) on the acyl ligand.

Formation of CO_2 : The Water Gas Shift Reaction. CO_2 was observed as a minor product (10%) in the reaction of **1** with CO . It is probably produced in a water-gas shift reaction, by nucleophilic attack of a hydroxyl ligand on coordinated CO . This leads to the formation of a hydroxycarbonyl ligand, which eliminates CO_2 . This chemistry is well-known for both homogeneous and supported rhodium catalysts.⁴⁸

Comparison with Homogeneous Chemistry. Several of the surface reactions described here were also observed in the reaction of the model compound, $[\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_2\text{Cl}]_2$, with CO . In addition, the $\eta^3 \rightarrow \eta^1$ allyl ligand shift induced by coordination of CO was directly observed by IR and ^{13}C NMR, eq 10. Reductive elimination of 1,5-hexadiene or insertion of CO to give an acylrhodium complex follows. The latter eliminates 1,6-

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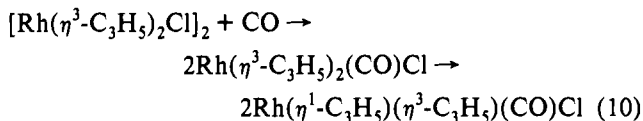
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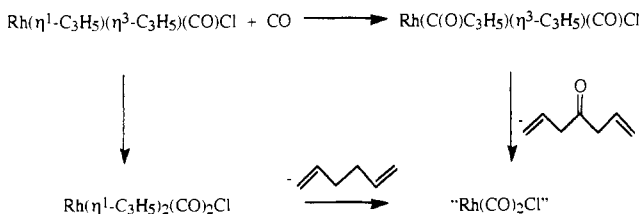
(47) Volger, H. C.; Vrieze, K. *J. Organomet. Chem.* **1968**, *13*, 479-493.

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heptadien-4-one with formation of the dicarbonylrhodium(I) product, Scheme 1.

Scheme 1



Interaction of Surface Complexes with H₂. The allyl, acyl, and carboxylate species disappear during treatment with H₂ followed by vacuum, leaving only alkyl and ester species on the surface. The acylrhodium(III) species **12** undergoes hydrogenation with elimination of *n*-butyraldehyde from the coordination sphere of Rh, consistent with the disappearance of the peak at 1692 cm⁻¹. The *n*-butyraldehyde is weakly physisorbed on silica and readily removed by exposure to dynamic vacuum, as demonstrated with an authentic sample. The sensitivity of acyl ligands on supported Rh catalysts to H₂ has been noted.⁴⁵ Thus hydrogenation of silica-supported (propanoyl)rhodium was reported to give physisorbed propanal.⁴³

The bidentate carboxylate species undergoes slow elimination of the carboxylate ligand from the coordination sphere of Rh. The ν(CO₂) bands eventually disappear after 48 h under H₂, Figure 5. At this point, only the hydrogenated silyl ester (derived from **6**) remains on the surface, as judged by the presence of alkyl and ester vibrations. Its ν(CO) band shifts from 1747 cm⁻¹ (on SiO₂₍₄₀₀₎) to 1713 cm⁻¹ under H₂, due to increased H-bonding to silanols produced in reaction 11, below. However, under dynamic vacuum at room temperature, this band returns to the higher frequency as water is eliminated from the surface. Thus organic ligands coordinated to Rh are removed by treatment with H₂, but organic fragments which have been transferred to the silica surface are stable under H₂. The interaction of **5** with H₂ leads to the formation of small metallic particles of Rh (see below).

Mobility of Dicarbonylrhodium(I) Fragments. In all cases, on silica, titania, and alumina, the primary Rh product from the reaction of **1**, **2**, or **3** with CO is monomeric, as shown by the presence of two ν(CO) bands in the IR spectra, Figure 6a, and six ν(CO) bands in the presence of a ¹²CO/¹³CO mixture. On silica, the angle between CO ligands, calculated from the integrated intensity ratio of the symmetric and asymmetric ν(CO) bands, is 80°. The ν(OH) band at 3636 cm⁻¹ on silica corresponds to a silanol ligand coordinated to **4b**, similar to **1b**.⁸

On the surface of silica, **4** dimerizes, as shown in eq 3. During this reaction, the distinctive ν(OH) band for coordinated silanol disappears. The ν(CO) bands shift and a third ν(CO) band, at higher frequency, appears, Figure 6b. The latter is typical of nonplanar dicarbonylrhodium dimers. The close correspondence between the experimental and calculated spectra of **5** in the presence of a ¹²CO/¹³CO mixture is evidence for its dimeric nature. A probable structure for **5** contains bridging siloxy ligands,⁵⁰ as in the molecular complex [Rh(CO)₂(μ-O-SiMe₃)]₂. This coordination mode for siloxy ligands on the silica surface has been demonstrated for the supported clusters Os₃(CO)₁₀(μ-H)(μ-O-Si≡).⁵¹ From the spectrum of **5**, Figure 6b, we calculate⁴⁹ the

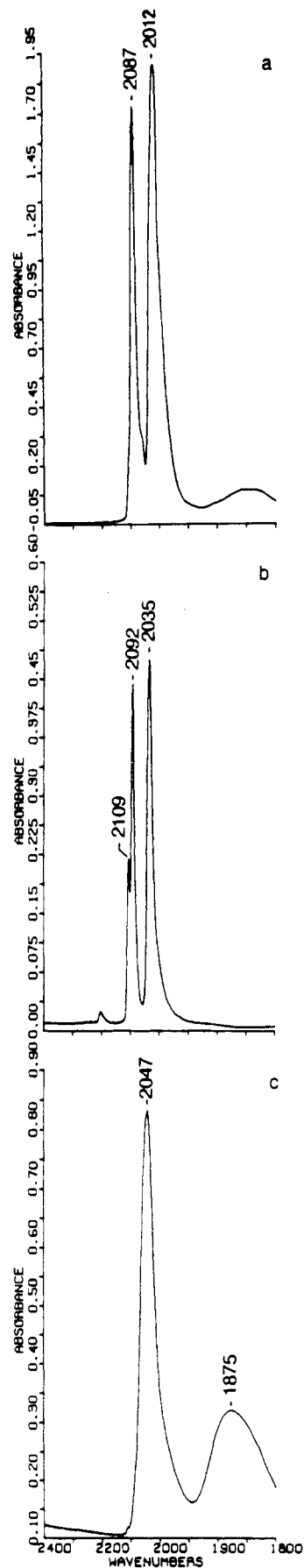


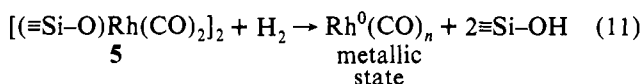
Figure 6. Mobility of surface rhodium species followed by the evolution of the ν(CO) bands in the infrared spectra: (a) monomeric (≡SiO)-(≡SiOX)Rh^I(CO)₂, **4**; (b) dimeric [(≡SiO)Rh^I(CO)₂]₂, **5**; (c) small metal particles, Rh⁰(CO)_{*n*}.

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angle between *gem*-CO ligands to be 80.5° and the dihedral angle between Rh^I(CO)₂ fragments to be 110.5° (compared to 91 and 124°, respectively, for [Rh(CO)₂Cl]₂).⁵² Bonding to adjacent siloxy ligands on the silica surface apparently imposes some constraints on the geometry of **5**.

Dimerization requires migration of Rh^I(CO)₂ fragments, a process which has been demonstrated on oxide surfaces during the formation of zerovalent Rh clusters.^{18,53} The presence of surface hydroxyl groups is thought to be crucial to the mobility of the dicarbonylrhodium fragments.⁵⁴

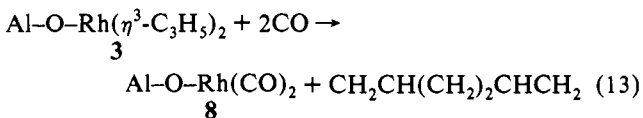
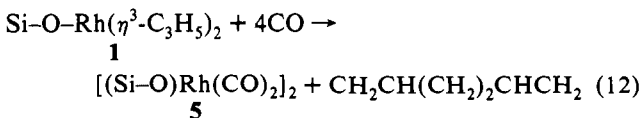
The interaction of **5** with H₂ leads to the appearance of broad ν(CO) bands at 2047 and 1875 cm⁻¹, Figure 6c. The positions of these bands are characteristic of terminal and bridging CO coordinated to metallic Rh,⁵⁵⁻⁵⁷ as is the shift of the ν(CO) bands to lower frequencies with decreasing CO coverage due to exposure to dynamic vacuum. The positions and intensities of these bands are dependent on particle size⁵⁸ and CO coverage.^{33,59} The observed particle size, 2–4 nm, is consistent with formation of small aggregates of Rh atoms. A sharp increase in the concentration of H-bonded silanols occurs concurrently with the formation of Rh crystallites, due to reduction of **5** by H₂, eq 11.



This reaction has been studied in detail on silica and alumina.⁵⁴ Generation of isolated OH groups was correlated with the reduction of Rh^I(CO)₂ by gaseous H₂ at temperatures above 200 K.⁵⁴ Aggregation of atomically dispersed Rh^I sites was reported to form crystallites of CO-covered metallic Rh⁰.

Reactions on Titania and Alumina. The behavior of **2** and **3** under CO is different from that of **1**. On both dehydroxylated alumina and titania, there is no reaction between the allyl ligands and surface hydroxyl groups, resulting in the absence of formation of propene. This can be explained by the lower density of surface hydroxyl groups remaining after the grafting of **2** and **3**. Therefore the formation of 1,5-hexadiene is kinetically favored over other possible processes. On both Al₂O₃₍₃₀₀₎ and TiO₂₍₂₅₀₎, a monomeric Rh^I(CO)₂ species is formed. This too is consistent with the hypothesis that surface hydroxyl groups are required for migration and dimerization of dicarbonylrhodium(I) fragments.

Comparison with Previous Work. Two reports on the reaction of oxide-supported bis(allyl)rhodium(III) with CO have appeared in the literature. Foley et al. found that **1**/SiO₂₍₂₀₀₎ does not react with CO.⁷ This conclusion was based on solid-state ¹H NMR evidence, in which a broad resonance at 1.2 ppm attributed to **1** did not change during interaction with CO. Also, elemental analysis of the surface after reaction revealed a large amount of remaining C, assumed to be due to allyl ligands still coordinated to Rh. In contrast, a study by McNulty et al. found that the interaction of **1**/SiO₂₍₂₀₀₎ and **3** with 1 atm of CO gives uniquely 1,5-hexadiene, as in eqs 12 and 13.¹² The formation of the dimer



5 on silica was suggested as evidence for a dimeric structure for **1** on silica.⁶⁰ Both laboratories (and ours) report that the reaction of **1** with CO gives three well-resolved ν(CO) bands on silica corresponding to the dicarbonylrhodium(I) dimer, **5**, regardless of the origin of the silica, its pretreatment protocol, or the CO pressure.

Our results appear to resolve the apparent discrepancy in the literature arising from the conflicting reports about the reactivity of **1** toward CO. Depending on the reaction conditions (primarily hydroxyl content), complete dealkylation of the surface with evolution of 1,5-hexadiene is only one of the possible reaction pathways. Alkyl groups may remain on the surface as monoallyl, acyl, and carboxylate ligands on Rh and the silyl ester **6** on silica, all of which are stable under CO. ¹H NMR spectroscopy of **1** does not reveal these reactions because of the overwhelming contribution of the ≡SiOH protons to the observed signal. In fact, Fischer et al. recently demonstrated that quantitative deuteration of the silica support is required to distinguish the ¹H CRAMPS NMR spectrum of **1** from the spectrum of ≡SiOH.⁹ After deuteration, the spectrum of **1** consists of a very broad resonance centered at δ = 5 ppm. Thus in Foley's experiment, the reaction of **1** with CO likely occurred but was not revealed by ¹H NMR. Our observation of the monomer **4** which eventually dimerizes to **5** (with a mobility which is likely to depend on surface hydroxyl content) eliminates the need to postulate a dimeric structure⁶⁰ for **1**.

Another apparent discrepancy in the literature is the reactivity of **5** toward H₂. Foley et al. observed no reaction between **5** and H₂, after a contact time of 15 min.⁷ No⁶¹ or little⁶² reaction with H₂ was observed for Rh^I(CO)₂ prepared by oxidative degradation of oxide-supported Rh metal particles in the presence of CO. McNulty et al. reported that the reaction of **5** with H₂ leads to the appearance of broad bands at 2044 and 1875 cm⁻¹ after 5 days under H₂.¹² This spectrum was assigned to higher nuclearity aggregates of Rh^I(CO)₂ containing bridging CO ligands. H₂ was suggested to facilitate migration of low-nuclearity surface fragments. Basu et al. reported that the reaction of atomically-dispersed alumina- and silica-supported Rh^I(CO)₂ with H₂ gives zerovalent Rh particles accompanied by the formation of surface hydroxyl groups.⁵⁴

We have observed that the reaction of **5** with H₂ is fairly slow, being complete only after 48 h under our experimental conditions (room temperature). CO is known to exert a strong disruptive effect on supported Rh crystallites, giving rise to isolated Rh^I(CO)₂ species which resist agglomeration under H₂.^{54,63,64} Therefore the absence of any observable reaction in 15 min, reported by Foley et al., is understandable. After prolonged exposure to H₂, our IR spectrum in the ν(CO) region consists of two broad bands at 2047 and 1875 cm⁻¹ (Figures 5 and 6b), nearly identical to the bands at 2045 and 1875 cm⁻¹ reported by McNulty et al.¹² Our interpretation of this spectrum differs from that of McNulty et al. but agrees with previous studies of metallic Rh supported on silica (terminal, 2040–2065 cm⁻¹; bridging, 1870–1900 cm⁻¹)⁶⁵ and single-crystal Rh surfaces.⁶⁶ The generation of silanol groups in the presence of H₂ is attributed to the formation

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of protons in the reduction of Rh^{I} by H_2 , according to eq 11 and in agreement with Basu et al.⁵⁴

Conclusion

The interaction of 1–3 with CO leads to the formation of oxide-bound $\text{Rh}^{\text{I}}(\text{CO})_2$. However, by varying the density of surface hydroxyl groups (via the degree of dehydroxylation of the oxide support and Rh coverage), we have discovered another organometallic aspect of this chemistry. We infer the interconversion $\eta^3\text{-C}_3\text{H}_5 \rightleftharpoons \eta^1\text{-C}_3\text{H}_5$ which is directly analogous to a process in molecular chemistry. When there are few surface hydroxyl groups, reductive elimination of the η^1 -allyl fragments occurs with formation of 1,5-hexadiene. Otherwise, the allyl ligands react directly with carbonyl and hydroxyl ligands. In this case, propene is formed by reaction of the allyl ligand with a proton which probably originates in a silanol ligand coordinated to Rh. CO insertion into an η^1 -allyl ligand gives an acyl ligand, which may undergo reductive elimination with another allyl ligand to give 1,6-heptadien-4-one. Alternately, the acyl ligand may migrate onto an oxygen atom of silica to give a silyl ester. Silanol-assisted migration of the dicarbonylrhodium(I) fragment leads to dimerization and, in the presence of H_2 , aggregation to small metal particles. On alumina and titania, the surface chemistry is much simpler, due to the lower concentration of hydroxyl groups. On these two oxides, the only observed reaction is coupling of the allyl ligands to give 1,5-hexadiene with formation of the dicarbonylrhodium(I) monomer.

Experimental Section

General Methods. The techniques of surface organometallic chemistry, in particular *in situ* experiments, have already been described.⁸ They involve sublimation of $\text{Rh}(\text{allyl})_3$ onto the chosen support which has been pretreated at the desired temperature for 16 h. All experiments were performed in the absence of solvent, in a high-vacuum system (10^{-5} Torr). The use of breakseal techniques avoids any possible contamination of surface complexes by air.

Supports. Two types of silica were used for the infrared and volumetric studies: Degussa Aerosil 200 and Shell S980 B1.5. The Degussa silica, with a specific surface area of $200 \text{ m}^2/\text{g}$, was compressed ($100 \text{ kg}/\text{cm}^2$) and then ground in an agate mortar. The Shell silica was manufactured as spheres having a diameter of 1.5 mm, a porous volume of $1.3 \text{ cm}^3/\text{g}$, and a surface area of $350 \text{ m}^2/\text{g}$. The pores have a diameter of 20 nm and allow easy access of most reactants. The titanium dioxide Degussa 25, used throughout this work, has a low specific surface, estimated at $50 \text{ m}^2/\text{g}$. X-ray data indicate that it is ca 80% anatase and 20% rutile. Degussa C alumina, $100 \text{ m}^2/\text{g}$, was compressed ($100 \text{ kg}/\text{cm}^2$) and then ground in an agate mortar. Rhone-Poulenc GFS C 200 alumina, with a surface area of $230 \text{ m}^2/\text{g}$, was pressed as 2-mm-thick pellets.

Pretreatment of Supports. Before sublimation of $\text{Rh}(\text{allyl})_3$, the oxides were treated by slow heating in air to $400 \text{ }^\circ\text{C}$. The surface was then treated alternately under oxygen (4 h) and under vacuum (10^{-5} Torr, 20 min) several times to degas the support, eliminate adsorbed molecular water and carbonates, and oxidize adsorbed hydrocarbons. The oxides were rehydrated by contact with water vapor at $25 \text{ }^\circ\text{C}$ (22 Torr, 4 h) and then placed under vacuum (10^{-5} Torr, 16 h) at the desired temperature between 25 and $550 \text{ }^\circ\text{C}$. This method allows reproducible control of the concentration of water and hydroxyl groups on the oxide surfaces.

Formation of 1–3. $\text{Rh}(\text{allyl})_3$, synthesized as described in the literature,⁶⁷ was introduced into a tube which had been degassed and filled with argon. This tube was then degassed under vacuum with liquid nitrogen and then isolated by sealing with a torch. The tube was fixed to the *in situ* IR cell. After preparation of the support (see above) and sealing of the IR cell, the breakseal connecting the tube containing $\text{Rh}(\text{allyl})_3$ and the cell was broken. $\text{Rh}(\text{allyl})_3$ was sublimed onto the support under vacuum without exposure to air. Analysis for Rh content was performed at the end of the experiment.

Reaction of 1–3 with CO. The introduction of CO into the IR cell was achieved by attaching the cell to a high vacuum line. The latter was connected to standard high-vacuum volumetric equipment and a quadrupole mass spectrum analyzer. The gaseous products were separated on a Porapak (R) column at $50 \text{ }^\circ\text{C}$, with H_2 as the carrier gas. A methanation oven (Ni/MgO, $350 \text{ }^\circ\text{C}$) was inserted between the column and the flame ionization detector to transform CO and CO_2 into CH_4 in the presence of H_2 . IR spectra were recorded on a FT-Nicolet 10-MX spectrophotometer.

Homogeneous Reaction. $[\text{Rh}(\text{allyl})_2\text{Cl}]_2$ was prepared according to the literature procedure.⁶⁷ The reaction with CO was followed by FT-IR (bubbling CO through the solution) and $^1\text{H NMR}$ (in a sealed tube under 1 atm of CO) in CDCl_3 at $-60 \text{ }^\circ\text{C}$. Gaseous products were determined on a CPSIL5 capillary column isothermal at $30 \text{ }^\circ\text{C}$.

Electron Microscopy. Conventional transmission electron microscopy was performed using a JEOL 100 CX electron microscope. Samples were examined both dry and after dispersion in ethanol followed by solvent evaporation.

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Supplementary Material Available: Text providing derivations of equations for calculation of CO force constants, coupling constants, and stretching frequencies in $^{12}\text{CO}/^{13}\text{CO}$ mixtures (4 pages). Ordering information is given on any current masthead page.

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