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Surface Organometallic Chemistry: Reaction of Tris-Allyl Rhodium with Surfaces of Silica, Alumina, Titania, and Magnesia

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Abstract: The reaction of $Rh(\eta^3\text{-}C_3H_5)_3$, **1**, with silica, alumina, titania, and magnesia has been followed by infrared spectroscopy, isotopic labeling experiments, quantitative analysis of gaseous products, and elemental analysis. Complex **1** reacts rapidly with alumina pretreated to 350 °C and with silica and titania to form a bis-allylic rhodium species grafted to the surface, but no immediate reaction was observed between **1** and alumina pretreated to 200 °C or magnesia. This reaction likely proceeds via electrophilic cleavage of Rh–C bonds of **1** by a surface OH group. On silica, the results of IR experiments after labeling the surface with ^{16}O–D and ^{18}O–H and structural arguments suggest that two 18-electron species are possible on the surface: one for which the rhodium is coordinated both to an oxygen and a hydroxyl group linked to the same silicon atom and another for which the oxygen atom and the OH group are linked to two different silicon atoms. Molecular mechanics modeling of silica, alumina, and titania was used as a complement to the experimental work to test the plausibility of various modes of attachment of the rhodium allyl complex.

Introduction

Surface organometallic chemistry is a field of increasing importance in heterogeneous catalysis.[1] One of the objectives of research in this field is to study elementary steps of heterogeneous catalysis. For this purpose, it is necessary to prepare stable reaction intermediates, e.g., π-allyl, σ-alkyl, carbene, etc. Reaction of organometallic compounds with surfaces of oxides may lead to intermediates in which an organometallic fragment remains coordinated to surface atoms. If a single structure or several closely related structures are formed on the surface, then it becomes possible to use stoichiometric reactions to characterize the reactivity of these surface species. By studying these grafted organometallic species, we can gain insight about the reactivity, the "working site", of some supported catalysts.

η^3-Allylic ligands are often considered as intermediates in catalytic reactions such as isomerization and oxidation of olefins.[2] It is interesting, therefore, to study in detail the reactivity of coordinated π-allylic ligands as a model for these catalytic reactions. In this, the first paper of a series, we will present the results of our studies of the chemisorption of $Rh(\eta^3\text{-}C_3H_5)_3$ on the surface of silica, alumina, titania, and magnesia. In the papers that follow, we will consider the stoichiometric reactivity of the grafted organometallic species derived from **1** with H_2, CO, and PMe_3.

Contradictory results have been published regarding the reaction occurring between **1** and various oxides. Tris(η^3-allyl)rhodium, $Rh(\eta^3\text{-}C_3H_5)_3$, was first synthesized by Shaw and co-workers in 1966.[3] In 1980, Ward et al.[4,5] reacted **1** with a silica surface in hexane at room temperature. After determining the number of moles of evolved propene, they proposed the following reaction:

$$\mathrm{{>}Si{-}OH + Rh(\eta^3\text{-}C_3H_5)_3 \rightarrow {>}Si{-}O{-}Rh(\eta^3\text{-}C_3H_5)_2 + C_3H_6} \tag{1}$$

This result has since been suggested to occur on several other oxides, specifically, alumina,[6] titanium dioxide,[7,8] and zeolites.[9]

In 1983, Foley et al.[10] questioned the silica results of Ward et al.[4,5] They concluded that only a fraction of $Rh(\eta^3\text{-}C_3H_5)_3$ reacted according to eq 1, while another fraction reacted according to eq 2:

$$\mathrm{3\,{>}Si{-}OH + Rh^{III}(\eta^3\text{-}C_3H_5)_3 \rightarrow ({>}Si{-}O)_3Rh^{III} + 3\,C_3H_6} \tag{2}$$

The stoichiometry of eq 2 was not supported by experiments measuring the amount of evolved propene. Only IR and chemisorption studies suggested the existence of the species $({>}Si{-}O)_3Rh^{III}$. Furthermore, Iwasawa and Sato[11] proposed another stoichiometry based on their studies of the reaction of **1** with TiO_2; they suggested the equation

$$\mathrm{2\,{>}Ti{-}OH + Rh(\eta^3\text{-}C_3H_5)_3 \rightarrow ({>}Ti{-}O)_2Rh(\eta^3\text{-}C_3H_5) + 2\,C_3H_6} \tag{3}$$

The stoichiometry of eq 3 was deduced from analysis of the pyrolysis products of the surface organometallic fragment. The amount of propene evolved was not determined.

Since there are conflicting results from different investigations, and given the possible importance of η^3-allyl rhodium complexes in rhodium hydride synthesis and alkane activation,[12] we felt it necessary to study the reactions of **1** with various oxides under well-controlled conditions using the methodology developed in our laboratory.[13] Specifically, the objectives of this work are the determination of the molecular environment of the rhodium atoms on the surface, i.e., the number of allylic fragments and oxygen atoms coordinated to the rhodium atom, and whether the surface organometallic fragment adopts a 16- or 18-electron configuration on the surface.[14]

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Table I. Spectroscopic Characteristics of $Rh(\eta^3\text{-}C_3H_5)_3$ and $[Rh(\eta^3\text{-}C_3H_5)_2Cl]_2$ Derivatives in the 4000–1200-cm^{-1} Region[a]

	type of vibration						
complex	ν(C–H)	ν(C–H)	ν(C–H)	ν(C–H)	δ(CH$_2$)	δ(CH$_2$)	ν(C–C–C)
$Rh(C_3H_5)_3/CCl_4$	3068 s	3007 vs	2956 w	2929 w	1487 m	1459 m	1387 m
$Rh(C_3H_5)_3/KBr$	3061 m	3000 m			1484 m	1456 m	1382 m
$[Rh(C_3H_5)_2Cl]_2/KBr$	3091 vw	3021 vw	3056 m	2992 m	1501 vw	1459 m	1391 m
$[Rh(C_3H_5)_2Cl]_2/CCl_4$	3088 vw	3020 vw	3056 m	2986 m	1500 vw	1460 m	1391 m
$Rh(C_3H_5)_3/SiO_2$[b]	3063 vs	3004 vs	3044 vs	2990 vs	1488 m	1461 m	1390 m
$Rh(C_3H_5)_3/SiO_2$[c]			3048 vs	2988 vs	1496 vw	1462 m	1391 m

[a] Very similar results have been obtained by the reaction of **1** with a silica$_{(25)}$, silica$_{(100)}$, silica$_{(200)}$, silica$_{(300)}$, silica$_{(400)}$, and silica$_{(500)}$. [b] During sublimation. [c] Under vacuum.

Table II. Spectroscopic Characteristics of $Rh(\eta^3\text{-}C_3H_5)_3$ and $[Rh(\eta^3\text{-}C_3H_5)_2Cl]_2$ Derivatives in the 1050- to 800-cm^{-1} Region

	type of vibration						
complex	ρ_t(CH$_2$)	ρ_t(CH$_2$)	ρ_w(CH$_2$)	ρ_w(CH$_2$)	ρ(CH$_2$)	ρ_r(CH$_2$)	ρ_r(CH$_2$)
$Rh(C_3H_5)_3/KBr$	1005 865 w	985 m	930 w	910 w		898 m	886 m
$[Rh(C_3H_5)_2Cl]_2/KBr$	998	965	929 w	915	903		
$Rh(C_3H_5)_3/SiO_2$[a]	992	955		913	900		

[a] Under vacuum at room temperature.

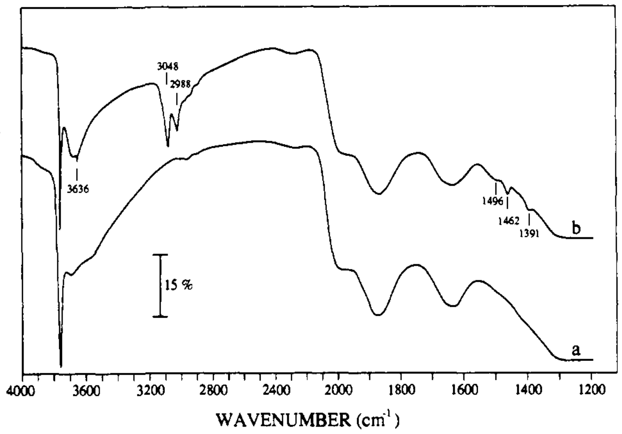

Figure 1. Infrared spectra of (a) silica$_{(200)}$; (b) silica$_{(200)}$ after sublimation of **1** at room temperature under vacuum and elimination of the propene under vacuum (10^{-5} Torr).

Results

Interaction of Tris-Allyl Rhodium with Partially Dehydroxylated Silica. The reaction of **1** with silica$_{(200)}$ was followed by Fourier transform IR (FTIR) spectroscopy and quantitative analysis of the products. Throughout the remainder of the text, the subscript after the name of an oxide indicates the temperature at which it was pretreated under vacuum. For example, in this case the silica was pretreated at 200 °C. At room temperature, **1** reactive (after sublimation) with the initially white silica$_{(200)}$ to give product **2** which was deep yellow. The FTIR spectra of the silica before and after the reaction are shown in Figure 1. The difference of these two spectra is shown as spectrum a of Figure 2. The FTIR spectra of $[(Rh(\eta^3\text{-}C_3H_5)_2Cl]_2$ (b) and $Rh(\eta^3\text{-}C_3H_5)_3$ (c) are also shown in Figure 2 for reference. The mode assignments for both the grafted species and the model compounds are summarized in Tables I and II.

Figure 3 shows an enlargement of the portion of the IR spectrum that corresponds to the C–H stretching bands. Initially this silica does not exhibit any bands corresponding to ν(C–H) vibrations, but **2**, spectrum c, showed two strong ν(C–H) bands at 3048 and 2988 cm^{-1}. The frequencies of these two bands were very similar to those observed for the model compound $[(Rh(\eta^3\text{-}C_3H_5)_2Cl]_2$ (Table I). Note that the two weak bands at 3091 and 3021 cm^{-1} of the model compound $[Rh(\eta^3\text{-}C_3H_5)_2Cl]_2$ were not resolved in the spectra of the species bound to the surface. Spectrum b of Figure 3 was obtained during the first minutes of the sublimation. The bands at 3063 and 3004 cm^{-1} were consistent with the existence of unreacted $Rh(\eta^3\text{-}C_3H_5)_3$ on the surface, since similar bands were found in the reference spectrum of the starting material. Since these bands are distinct from those of the grafted

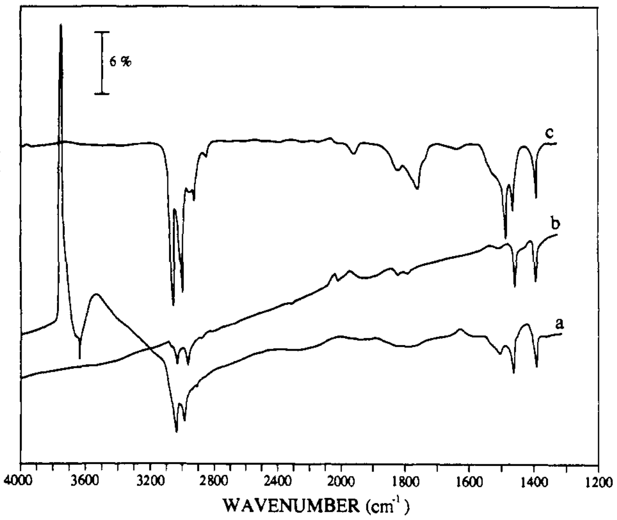

Figure 2. (a) Infrared difference spectrum of the spectra in Figure 1, b – a; (b) spectrum of $[Rh(\eta^3\text{-}C_3H_5)_2Cl]_2/KBr$; (c) spectrum of $Rh(\eta^3\text{-}C_3H_5)_3/KBr$.

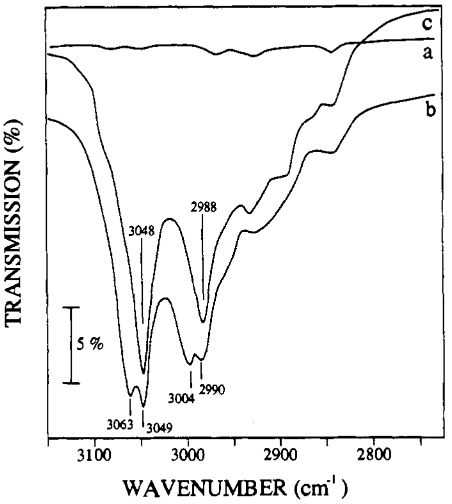

Figure 3. Infrared spectra in the ν(C–H) region during the chemisorption process of **1** (a) silica$_{(200)}$; (b) during the sublimation of **1** on silica, the physisorbed **1** and **2** are present; (c) after 5 min under vacuum (10^{-5} Torr) at room temperature, only **2** is present.

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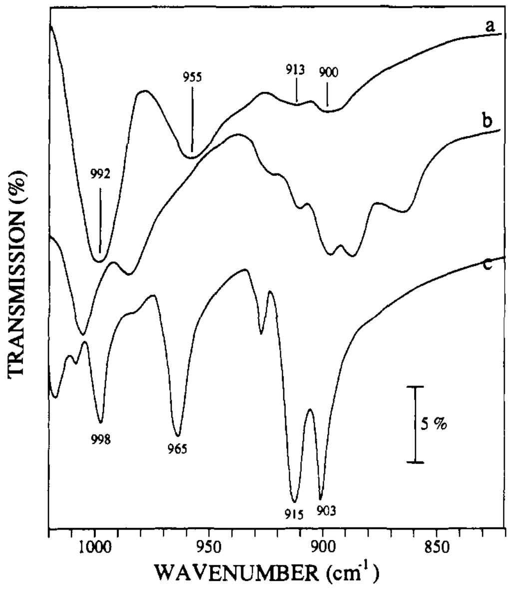

Figure 4. Infrared spectra in the $\rho(CH_2)$ region: (a) **2** on silica; (b) **1** on KBr; (c) $[Rh(\eta^3\text{-}C_3H_5)_2Cl]_2$/KBr.

complex and since they disappear after evacuation, we concluded that there was not a large excess of the unreacted starting material left on the surface.

Product **2** was also tentatively characterized by bands in the 1500–1300- and 1020–850-cm^{-1} regions which were similar to those for the model $[Rh(\eta^3\text{-}C_3H_5)_2Cl]_2$.[15a] The bands at 1496 (w), 1462 (m), and 1391 cm^{-1} (m) can be assigned to $\delta(CH_2)$ and ν(C–C–C) modes of the allyl ligands. Although the bands of **2** in the 1020–850-cm^{-1} region, Figure 4, were broader than the corresponding bands of $[Rh(\eta^3\text{-}C_3H_5)_2Cl]_2$, the peak positions were very close,[15b] as shown in Table II. In particular, one should observe that the spectrum of $Rh(\eta^3\text{-}C_3H_5)_3$ had very different peak positions. In summary, the FTIR spectrum in these three regions indicates that **2** was not tris-allyl rhodium; the strong similarities between the spectrum to a bis-allyl rhodium model compound and that of **2** suggests that probably **2** is a bis-allylic species. As usual in surface science, one cannot rule out completely other possible interpretations since IR spectroscopy as many other techniques is a comparative and not an absolute technique.

Changes in the vibrational spectrum in the O–H stretching region indicated that the rhodium complex likely reacted with the O–H groups on the surface of the silica. Initially, the silica showed two vibrational bands in the 4000–3500-cm^{-1} region, a sharp band at 3746 cm^{-1}, and a broad band at 3650 cm^{-1}. These bands have been assigned to ν(OH) vibrations of linear and hydrogen-bonded silanols, respectively.[16] After silica reacted with **1**, the intensity of the band at 3746 cm^{-1} decreased while the band due to hydrogen-bonded silanols changed shape and position. The difference spectrum shown in Figure 2a has a broad positive peak at 3580 cm^{-1} and a broad negative peak centered at 3680 cm^{-1}. The combination of these two changes may indicate that either the hydrogen-bonding structure was changed by the presence of the rhodium complex or that a new species was formed which has an O–H bond. The IR spectrum of silica$_{(550)}$ before and after reaction with **1** showed the formation of a braod band at ca. 3680 cm^{-1}, even though, the silica before reaction only exhibited a single vibrational band at 3747 cm^{-1} due to non-hydrogen-bonded silanol groups. This result indicates that a large fraction of the absorption near 3650 cm^{-1} was due to the grafted complex. An intriguing feature of the spectrum of silica after reaction with **1** is the formation of a sharp band of weak intensity at 3636 cm^{-1}. During experiments in which increasing amounts of **1** were added to the sample, an increase in the intensity of this band was observed; thus it was likely due to a hydroxyl group coordinated to rhodium. A band of similar frequency has also been previously reported for a hydroxyl group coordinated to a metal center.[17] The identity of this species will be further discussed below in the context of molecular modeling.

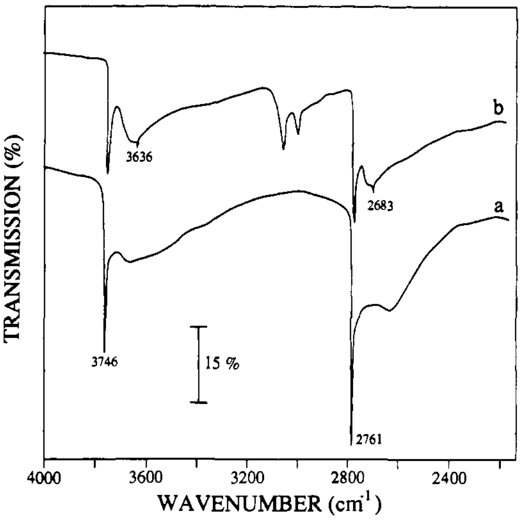

Figure 5. Infrared spectra in the ν(OH) or ν(OD) region: (a) partially deuterated silica; (b) after sublimation of **1** on the same deuterated silica for 1 min followed by evacuation.

Since we hypothesized that some of the silanols with vibrational bands near 3650 cm^{-1} were due to those coordinated with the rhodium complex, isotopic labeling experiments were conducted for confirmation. Before isotopic exchange, silica$_{(200)}$ showed two ν(OH) bands: those at 3746 cm^{-1} which are due to free silanols and those at ca. 3650 cm^{-1} which are due to silanol groups involved in hydrogen bonding.[16] After approximately 50% of the OH groups were exchanged with D_2O, the IR spectrum, Figure 5, showed two pairs of bands: ν(O–H) bands at 3746 and 3650 cm^{-1} and ν(O–D) bands at 2761 and 2700 cm^{-1}. Since the frequency ratios are 1.36 and 1.35 respectively, these peak positions are consistent with that predicted for isotopic substitution. After **1** reacts with this surface, a simultaneous reduction intensity of the ν(OH) and ν(OD) bands for the free silanol species was observed. When the reaction was followed by in situ IR spectroscopy, it was observed that the vibrations due to the ⪢Si–OH and ⪢Si–OD groups became less intense at the same rate, and thus they appear to have approximately the same reactivity toward the rhodium complex. The reduction in absorbance due to the silanol bands was accompanied by the development of two sharp bands at 3636 and 2683 cm^{-1}. These bands also had the expected isotopic frequency ratio for H/D substitution, and thus the species responsible for these bands involved coordination or reaction with surface hydroxyl groups.

Isotopic labeling experiments were also carried out using ^{18}O-enriched silica obtained by partial exchange of the surface silanols with $H_2{}^{18}O$. The spectra of the exchanged silica before and after reaction with **1** are shown in Figure 6. Bands consistent with the free silanol groups ⪢Si–^{16}OH and ⪢Si–^{18}OH were observed at 3748 and 3735 cm^{-1}, respectively. When **1** reacted with the surface, the vibrational bands associated with the free silanols disappeared, while the band associated with the hydrogen-bonded

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(15) (a) Chenskaya, T. B.; Leites, L. A.; Aleksanyan, V. T. *J. Organomet. Chem.* **1978**, *148*, 85. (b) The only difference between the spectrum of species **2** and the spectrum of the model compound $[(Rh(\eta^3\text{-}C_3H_5)_2Cl]_2$ is a very weak and broad shoulder at 1496 cm^{-1} which can be attributed to a very small amount of unreacted $Rh(\eta^3\text{-}C_3H_5)_3$ as already observed in Figure 3. This band is more intense at the beginning of the sublimation.

(16) (a) Van Roosmalen, A. J.; Mol, J. C. *J. Phys. Chem.* **1978**, *82*, 2748. (b) Ghiotti, G.; Garrone, E.; Morterra, C.; Boccuzi, C. *J. Phys. Chem.* **1979**, *83*, 2863. (c) Morrow, B. A.; Cody, I. A.; Lee, L. S. M. *J. Phys. Chem.* **1976**, *80*, 2761 and references therein. (d) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 1487.

(17) (a) Oliver, D.; Bonneviot, L.; Cai, F. X.; Che, M.; Gihr, P.; Kermarec, M.; Lepetit-Pourcelot, C.; Morin, B. *Bull. Soc. Chim. Fr.* **1985**, 370. (b) Peri, P. B. *J. Chem. Soc., Discuss. Faraday* **1966**, *41*, 121.

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Table III. Qualitative and Quantitative Analysis of the Gases Evolved during Reaction of **1** with Two Types of Silica Dehydroxylated at Various Temperatures

	SiO_2[b]	SiO_2[b]	SiO_2[c]	SiO_2[b]	SiO_2[b]
temp (°C)	100	200	300	300	500
C_3eq/Rh[a]	0.96 ± 0.05	1.06 ± 0.05	0.95 ± 0.05	0.96 ± 0.05	0.93 ± 0.05
molar composition (%)					
C_3H_6	98	99	99	99	99
C_3H_8	2	2	1	1	1

[a] Moles of C_3H_6 or C_3H_8 evolved per mole of Rh introduced. [b] Silica Aerosil from Degussa. [c] Silica S980 from Shell.

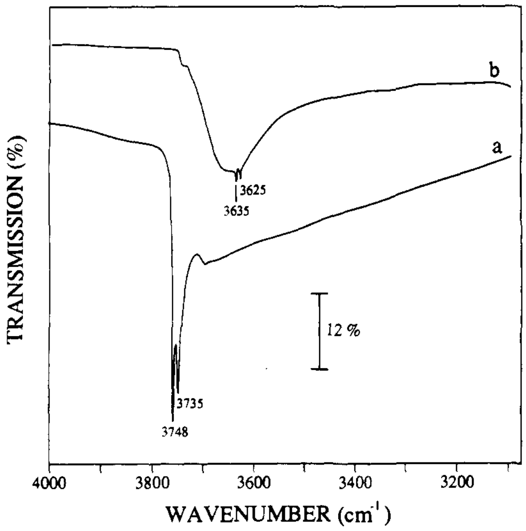

Figure 6. Infrared spectra in the ν(OH) region: (a) silica$_{(200)}$ enriched with $H_2{}^{18}O$; (b) after sublimation of **1** on the same labeled silica for 5 min followed by evacuation.

silanols increased in intensity. Furthermore, two sharp bands appeared at 3635 and 3625 cm^{-1}. The frequency of these sharp bands correspond to a calculated isotopic $\nu(^{16}OH)/\nu(^{18}OH)$ ratio of 1.003 as opposed to the theoretical value of 1.006. The reason that all the absorption due to the free silanols was eliminated during this experiment was unclear. It is possible that the amount of rhodium reacted was higher, since the sublimation technique used to study the reaction of $Rh(\eta^3\text{-}C_3H_5)_3$ with silica by IR did not permit precise control of the quantity of rhodium bound to the surface. However, the results shown in Figure 6 demonstrate that it was possible for all the free silanols to react and may indicate a higher reactivity of the free silanol groups.

In summary, **2**, in three different spectral regions corresponding to vibrations of the allyl ligands, gave the characteristic absorption bands of a $Rh(\eta^3\text{-}C_3H_5)_2$ fragment. Furthermore, in the region where stretching vibrations for silanol groups are found, **2** was distinguished by a significant reduction in the absorption due to free silanols and by the development of a new sharp band with a vibrational frequency of 3636 cm^{-1}.

The stoichiometry of the reaction of $Rh(\eta^3\text{-}C_3H_5)_3$ with two types of partially dehydroxylated silica was determined by sublimation of a known quantity of $Rh(\eta^3\text{-}C_3H_5)_3$ on silica in a closed vessel at room temperature. After equilibration the reaction was characterized by qualitative and quantitative analysis of all evolved gases by volumetric and chromatographic methods and analysis of the amount of fixed rhodium by elemental analysis. These results are given in Table III. For silica samples dehydroxylated at several different temperatures, and thus with different surface hydroxyl group concentrations, approximately 1 mol of propene per mol of rhodium was evolved. This stoichiometry was observed using both a nonporous Degussa silica (with a surface area of 200 m^2 g^{-1}) and a Shell silica (with a surface area of 350 m^2 g^{-1}). Since a constant propene/rhodium ratio was observed, it was likely that a simple reaction took place resulting in a single product. The observed products were not the result of a reaction with water. Three experimental observations excluded this possibility: (1) reaction of **1** with silica$_{(500)}$, which contains no molecular water, yielded 1 mol of propene per mol of rhodium; (2) **1**, when pure, did not react with water at 25 °C; (3) when an additional 1.5 mol of water per mol of rhodium was introduced to the sample, no further propene was evolved.

Table IV. Gas Obtained by Pyrolysis of **2**

temp intervals, °C	gas evolved	mmol	C_3eq
0–40	propene	0.196	1.06
40–100	propene	0.086	0.46
	propane	0.008	0.04
100–400	propene	0.000	0.00
	propane	0.112	0.61
	ethane	0.034	0.12
	methane	0.236	0.43
	CO_2	0.200	0.36
	$H_2 + CO$	0.001	0.00
		total	3.08

It was found that the quantity of rhodium fixed to the surface was sensitive to the dehydroxylation temperature of the silica. Silica$_{(25)}$, which was rich in molecular water, reacts only slowly with $Rh(\eta^3\text{-}C_3H_5)_3$ and resulted in only about 2% w/w of rhodium grafted to the surface. Up to 5.2% w/w of rhodium was grafted to silica$_{(300)}$ which corresponded to the consumption of three OH/100 Å^2 (assuming that each mole of **1** reacted with, or was coordinated to, two surface silanols). The lower number of grafted species on silica$_{(25)}$ compared to a silica$_{(300)}$ was consistent with the lower availbility of OH groups due to their coordination with molecular water.

The thermal stability of species **2** between 25 and 350 °C, was determined by sequentially heating the sample to higher and higher temperature. The evolution of gases after heating to various temperatures is summarized in Table IV. At 25 °C, after equilibrating for 48 h, 1 mol of propene per mol of rhodium was evolved. After holding the sample temperature at 50 °C for 100 h, a fraction of species **2** decomposed to give another 0.5 equiv of a mixture of propene and propane. The evolution of more than 1 mol of propene per mol of rhodium suggested that some of the bis-allyl species undergo reaction with a second OH group to give a mono-allyl species. Since at this point there were several species on the surface, accurate characterization was no longer possible.

While heating slowly from 50 to 350 °C, the remainder of the carbon was evolved. A total of 9.24 mol of carbon was obtained per mol of rhodium. Above 100 °C the main products were propane and lower alkanes, and the pellet became black, suggesting the presence of metal particles. This hypothesis was tested by the exposure of the sample to CO. Two broad bands appeared in the IR spectrum at ca. 1810 and 2050 cm^{-1}. These bands can be attributed to the ν(CO) mode of bridging and linearly bonded CO on rhodium metal particles.[19] When O_2 was added, these bands disappeared and CO_2 was detected in the gas phase. Furthermore, the formation of lower alkanes was likely the result of reactions occurring on reduced metal particles.[18] These experimental results all indicate the formation of rhodium particles on the surface during the pyrolysis of **2**.[19]

In summary, the IR spectra indicated the formation of a bis-allyl rhodium species on the surface and that some of the OH groups on the surface of silica were consumed. However, even during an experiment where all the free silanol groups were consumed, a large ν(O–H) band near 3600 cm^{-1} was observed in the spec-

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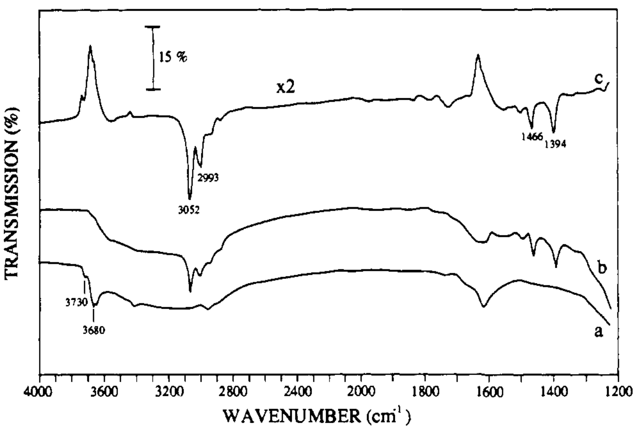

Figure 7. Infrared spectra of (a) $TiO_{2(250)}$; (b) after reaction with **1** followed by evacuation; (c) difference spectrum b − a.

trum. This suggests that some of the grafted complexes may have an O–H bond. A very sharp band was also observed in this region which was likely due to the formation of a small amount of a species with a unique structure. The quantitative analysis of the products of the reaction between **1** and silica suggested that a rhodium species, with two allyl ligands, was coordinated with the surface. Upon further heating, all of the carbon of the allyl groups was desorbed in the form of a mixture of alkenes, alkanes, and carbon dioxide. After heating the sample to 350 °C, metallic rhodium particles remained on the silica surface.

Interaction of 1 with Partially Dehydroxylated Titania. The reaction of **1** with a titania surface, dehydroxylated at 250 °C, was followed by IR spectroscopy. The white titanium dioxide gave, after reaction with **1** at room temperature, a yellow product **3**. The spectra of titania$_{(250)}$ before and after reaction with **1** as well as their difference are shown in Figure 7. The 3200–2800-cm^{-1} spectral region is initially free of ν(C–H) vibration bands. The product **3** is distinguished by two bands of medium intensity at 3052 and 2993 cm^{-1}. In the 1500–1200-cm^{-1} spectral region, two sharp bands at 1466 cm^{-1} (w) and 1394 cm^{-1} (m) were observed. These two sets of bands were similar in frequency and relative intensity to those of the model compound $[Rh(\eta^3\text{-}C_3H_5)_2Cl]_2$. Comparison of the difference spectrum of **3** shown in Figure 7c and the spectrum of **2** shown in Figure 2a showed that, in the regions associated with the vibrations of the allyl moieties, the two species exhibited nearly the same peak positions and relative intensities. Thus it was likely that a bis-allyl rhodium species was also formed on titania.

In the 4000–3500-cm^{-1} region, titania showed three ν(OH) bands at 3730, 3680, and 3660 cm^{-1}. These bands are consistent with previously reported spectra for titania.[20] These bands immediately and completely disappeared upon contact with **1**. The difference spectrum, Figure 7c, also indicated the development a weak broad band at 3500 cm^{-1} that may be due to a ν(O–H) mode of the grafted complex; however, the development of a very sharp band in this region was not observed after the reaction of **1** with titania.

Under experimental conditions similar to those described for silica, the reaction of **1** with $TiO_{2(250)}$ yielded only 0.6 mol of propene per mol of rhodium, but upon the addition of 1.5 mol of water, the additional 0.4 mol of propene was evolved. Since we have previously demonstrated that water does not react with **1** at 25 °C, we concluded that the introduction of water to $TiO_{2(250)}$ was responsible for the creation of extra (⋗Ti–OH) groups[21] which, in turn, reacted with **1** to yield more of the grafted complex and evolve more propene.

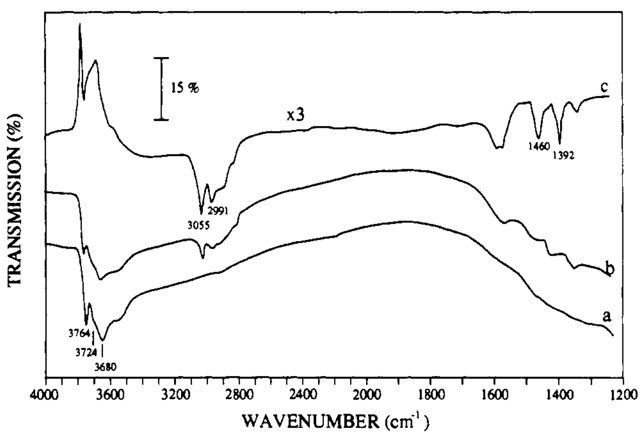

Figure 8. Infrared spectra of (a) $Al_2O_{3(300)}$; (b) after reaction of **1** at room temperature followed by evacuation; (c) the difference spectrum b − a.

In summary, in two IR spectral regions associated with the vibrations of allyl groups, **3** exhibited bands characteristic of a bis-allyl fragment. The reaction of **1** with titania resulted in the loss in intensity of the bands associated with the surface hydroxyl groups of titanium dioxide. Since the addition of water resulted in the formation of further propene, it was likely that the formation of the grafted species was limited by the availability of surface hydroxyl groups.

Interaction of 1 with Partially Dehydroxylated Alumina. The reaction of **1** at room temperature with initially white alumina$_{(350)}$ gave a yellow product **4**. The FTIR spectra of alumina before and after reaction with **1** as well as their difference are shown in Figure 8. In the 3200–2800-cm^{-1} region, which did not initially contain ν(C–H) vibrational bands, **4** exhibited two intense ν(C–H) bands, at 3055 and 2991 cm^{-1}. In the 1500–1200-cm^{-1} region, **4** exhibited bands at 1460 and 1392 cm^{-1}. These bands were similar to those seen for the model compound $[Rh(\eta^3\text{-}C_3H_5)_2Cl]_2$ and for the products of the reactions of **1** with silica and titania. Thus the IR spectrum indicated the formation of a bis-allyl rhodium species.

In the 4000–3500-cm^{-1} region corresponding to ν(OH) vibrations, alumina$_{(350)}$ initially exhibited three bands at 3764, 3680, and 3580 cm^{-1}.[20] The intensity of these did not diminish uniformly after reaction with **1**. The intensity of the two higher frequency bands decreased, as indicated by a positive peak in the difference spectrum; however, the lower frequency band remained unchanged. This band may be due to molecular water coordinated with the surface.[20]

The rate of reaction of **1** with alumina depended strongly on the pretreatment temperature. The spectrum of alumina$_{(200)}$, after the adsorption of **1**, exhibited only vibrational bands that could be attributed to either alumina, coordinated water, or unreacted **1**.

In summary, **4** in two spectral regions exhibits bands characteristic of $Rh^{III}(\eta^3\text{-}C_3H_5)_2$ fragment. Only a fraction of the hydroxyl groups disappeared, and no sharp peaks appeared in the OH stretching region of the spectrum.

When **1** reacted with the alumina$_{(350)}$ at room temperature, about 0.8 mol of propene evolved per mol of rhodium. When 1.5 mol of water was added per mol of compound **1**, an additional 0.2 mol of propene per mol of rhodium evolved. In total, 1 mol of propene per mol of rhodium was formed.

Despite the significant concentration of hydroxyl groups on alumina$_{(350)}$, only certain hydroxyl groups seemed to react with **1**.[22] Apparently, the reaction of traces of water with the alumina created more (⋗Al–OH) reactive sites, which allowed the reaction with **1** to go to completion, as observed for titania.

Interaction of 1 with Partially Dehydroxylated Magnesia. The interaction of **1** with a magnesia$_{(200-400)}$ was followed by IR spectroscopy and analysis of the evolved gases. The initially white

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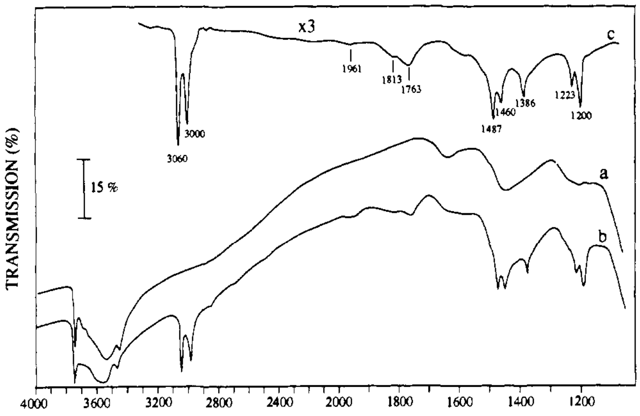


Figure 9. Infrared spectra of (a) $MgO_{(250)}$; (b) after sublimation of **1** at room temperature for several hours; (c) difference spectrum b − a.

magnesia rapidly became a very pale yellow. The IR spectra of magnesia after interaction with **1** and of **1** deposited on KBr were very similar, as shown in Figure 9.

When $magnesia_{(200)}$ was exposed to **1**, no gas was evolved during the first 4 h of interaction, and only vibrations characteristic of **1** and magnesia were observed. With other supports (TiO_2, SiO_2, Al_2O_3), the gases were evolved during the first minutes of interaction, and this evolution was essentially complete within several hours, if the number of surface hydroxyl groups was sufficient. After 60 h of interaction of **1** with magnesia, 0.72 mol of propene was obtained per mol of rhodium. After several days, the magnesia disk first became brown, then turned black, and the vibrations characteristic of **1** disappear and no new bands appear. These changes were likely due to the slow decomposition of **1** which produced metallic particles.

Molecular Modeling

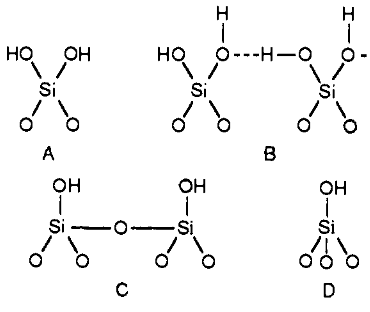
We have previously studied the accommodation of trinuclear osmium clusters on silica and alumina.[23] For this large cluster, it was observed that only certain sites on the surface allowed realistic Os–O bond distances and Os–O–Os and Os–H–Os angles without significant steric interactions between the atoms of the surface and of the cluster. In the case of the tris-allyl rhodium complex, however, since the removal of one allylic ligand opens two sites in the pseudo-octahedral coordination sphere of the metal and since it is a mononuclear complex, it is unlikely that many hydroxyl groups on the surface will be excluded by steric interactions between the bis-allyl rhodium fragment and the atoms of the surface. Thus the question to be answered by molecular modeling is not if the fragment can be accommodated on the surface but what kinds of local structures are consistent with the experimental data.

The experimental results described above suggest that a bis-allylic rhodium complex was produced by the reaction of **1** with hydroxyl groups on the surfaces of silica, titania, and alumina. The major gaseous product formed during this reaction at room temperature was propene; thus electrophilic cleavage of the Rh–C bond by surface OH groups resulted in the formation of a Rh–O bond and a 16-electron complex. However, given the widely observed propensity for bis-allyl rhodium to form 18-electron complexes, it is expected that, if a second hydroxyl group or other Lewis base is near enough to the rhodium center, it will be coordinated via a two-electron donor bond, as in the model compound $[Rh(\mu\text{-}OH)(\eta^3\text{-}C_3H_5)_2]_2$.[25] The possibility of formation of both a covalent bond and p-orbital donation with the same oxygen atom was also considered,[24] but extended-Hückel calculations of the O–Rh bond order of the bis-allyl rhodium complex indicated no significant donation of electrons from the p-orbitals.[14] The formation of a complex with a coordinated hydroxyl group was effectively observed. The FTIR spectra recorded after the reaction of **1** with both silica and titania showed the development of intensity ca. 3600 cm^{-1}. Hydroxyl groups datively coordinated to a metal center have been observed to exhibit OH stretching modes at 3549 and 3580 cm^{-1}.[25] An 18-electron structure was also proposed by Halet and Hoffmann.[14] Although they did not cite any experimental evidence supporting its existence, they proposed a "two-oxide-bound complex" would be possible on the (011) rutile face of hydroxylated titania. Their extended-Hückel calculations indicated that the 18-electron species may be energetically favored over the other surface complexes studied. A rhodium coordination sphere has also been reported for the model compound $[Rh(\mu\text{-}OH)(\eta^3\text{-}C_3H_5)_2]_2$.[25] The X-ray structure of this binuclear rhodium complex gives an O···O distance of 2.80–2.90 Å and Rh–O distances of 2.15–2.20 Å.

The calculations of Halet and Hoffmann[14] indicated that the electronic structure of the surface complexes and the chosen mononuclear analogue were very similar. Thus, it is unlikely that coordination with the surface significantly changed the structure around the rhodium atom. The task of modeling the surface structures was greatly simplified by assuming that the bond lengths and bond angles involving the rhodium atom were identical with the model compound $[Rh(\mu\text{-}OH)(\eta^3\text{-}C_3H_5)_2]_2$.[26]

Silica Support. We recently described a model for hydroxylated silica surface which was developed through the application of molecular mechanics and computer graphics.[23] It was based upon the work of others[16] who proposed that the silica surface, although heterogeneous, resembled that of hydroxylated β-cristobalite and related crystalline faces. Studies of hydroxylated silica suggest that the surface is heterogeneous and is probably composed of regions similar to the (100) face and the partially hydroxylated (111) face. The degree of hydroxylation is a function of the pretreatment temperature of the silica.[26]

Hydroxylation of the (100) surface leads to geminal $Si(OH)_2$ groups, A, which form hydrogen-bonded chains, B, through interaction with neighboring geminal groups. Sindorf and Maciel[16d] have recently quantified the number of geminal hydroxyl groups on silica surfaces using chemical modification and ^{26}Si NMR spectroscopy. They found that the number of geminal hydroxyl groups on silica surfaces varies between 12 and 24% depending on the treatment temperature. The dehydroxylation of this 100 surface is widely believed to occur by the reaction of OH groups on neighboring silicon atoms which results in the formation of a Si–O–Si siloxane bridge C:



Hydroxylation of the (111) surface gives isolated Si–OH groups, D. This structure is essentially a hexagonal array of hydroxyl groups with an average O–O distance of 5.0 Å.

Several possible local structures of the rhodium surface complexes considered are shown in Figure 10. Modeling of these structures was employed to gain insight as to how the $Rh(\eta^3\text{-}C_3H_5)_2$ fragment might be accommodated on local sites of hydroxylated silica. The procedure employed attempts to fit the organometallic fragment to local sites of silica surface which were generated in our previous work.[23]

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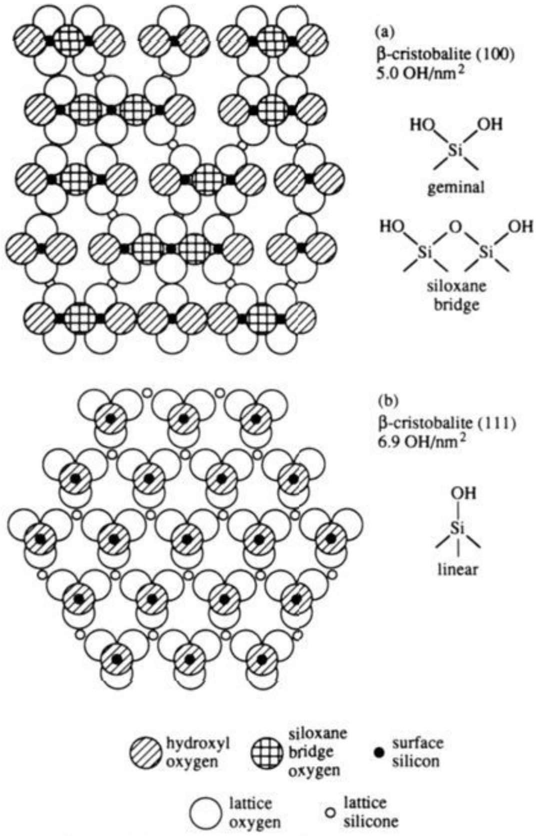

Figure 10. Some of the local structure for 18-electron bis-allyl rhodium complexes on the hydroxylated planes of β-cristobalite.

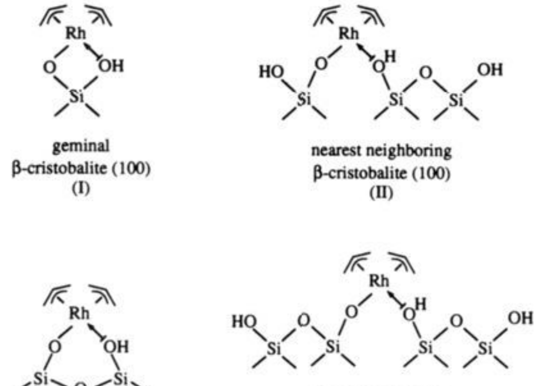

Figure 11. Structure of $((\mathrm{Rh}(\eta^3\text{-}C_3H_5)_2(\mu\text{-OH}))_2$ from the X-ray determination reported in ref 25. The hydrogen atoms positions have been inferred from the heavy atom positions.

Surface complexes were modeled by fitting the $\mathrm{Rh}(\eta^3\text{-}C_3H_5)_2$ fragment to local regions of surface. A hydrogen atom was removed from an OH group of a particular surface site, and the fragment $\mathrm{Rh}(\eta^3\text{-}C_3H_5)_2$ was attached to that oxygen and one other oxygen atom on the surface employing the Rh–O distances and the O–Rh–O angle of the model compound $[\mathrm{Rh}(\mu\text{-OH})(\eta^3\text{-}C_3H_5)_2]_2$ illustrated in Figure 11.[25]

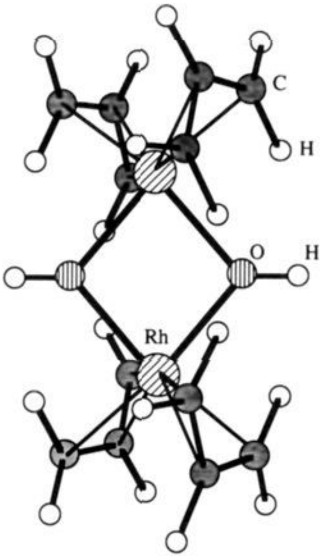

Figure 12. Ball-and-stick representation of surface complex I.

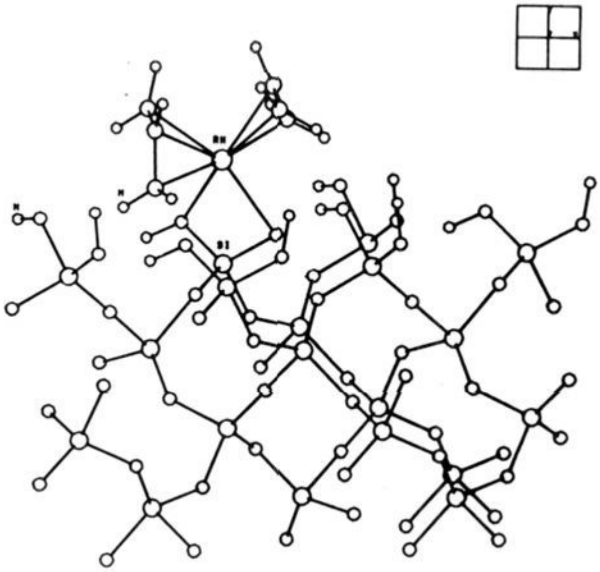

Figure 13. Ball-and-stick representation of surface complex II.

All of the nonbonded contact distances between surface atoms and $\mathrm{Rh}(\eta^3\text{-}C_3H_5)_2$ fragment atoms were calculated in order to determine if the fragment could be reasonably accommodated on the local surfaces sites. If the nonbonded contact distances between fragment atoms and surface atoms are larger than the sums of their van der Waals radii, we concluded that the rhodium fragment could be grafted onto that particular surface site. On the surface sites containing OH groups, rotation around the Si–O axes of Si–OH groups was allowed in order to avoid short contact between hydrogen atoms of OH groups and atoms of the organometallic fragment. We found that the $\mathrm{Rh}(\eta^3\text{-}C_3H_5)_2$ fragment could be accommodated on the (100) silica surface sites A and B to give surface complexes I and II, and the (111) silica surface site D to give surface complex III (Figure 10) without steric complications. On the other hand, complex IV derived from a siloxane bridge surface site C seems less likely because of apparently significant steric interactions between the allyl groups and the surface. Figures 12, 13, and 14 are ball-and-stick representations of I, II, and III derived using CHEMX graphics.[38b] This preliminary approach, while not offering proof of the structures of

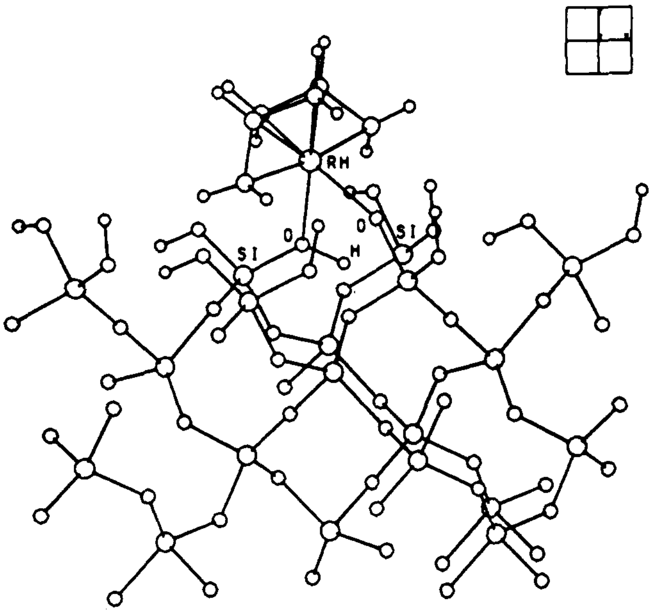

Figure 14. Ball-and-stick representation of surface complex III.

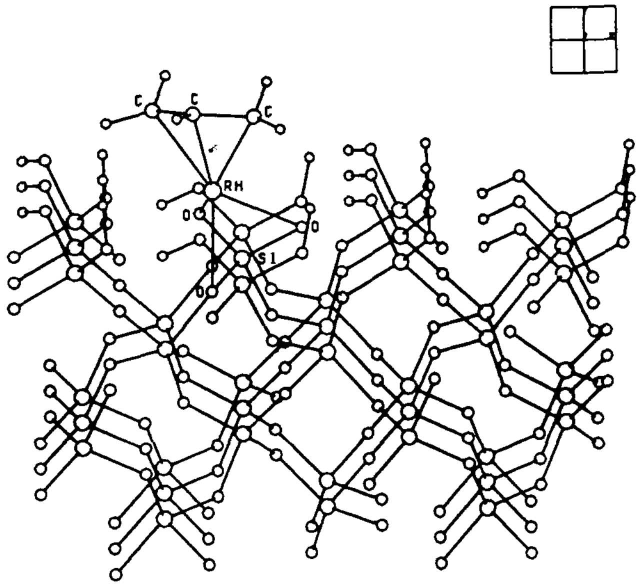

Figure 15. Ball-and-stick representation of surface complex V.

surface complexes, does indicate which of the proposed possibilities are more reasonable.

An intriguing feature of the FTIR spectra of the product resulting from the reaction of **1** and silica was the formation of a sharp band at 3636 cm^{-1}. The peak width of this band suggests it was the result of a species that exhibited vibrational modes more similar to a free molecule than a solid. Typically the vibrational bands exhibited by silica are broadened due to the wide range of local structures contributing to the same band. Of the structures illustrated in Figure 10, the complex with both the oxygen atom and hydroxyl group bonded to the same silicon atom, structure I, is a likely candidate for the species exhibiting this narrow band, since this four-membered ring structure will be the least influenced by the motions of the other atoms of the silica surface. The other structures illustrated in Figure 10 are less likely to exhibit sharp bands, since they are more strongly coupled to the motions of the lattice.

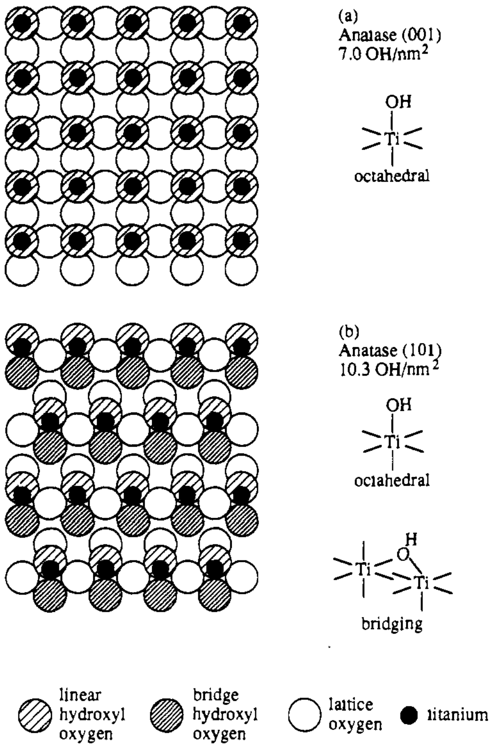

Figure 16. Representation of the surface structure of the fully hydroxylated (001) and (101) planes of anatase. The ionic radii of the atoms have been reduced to 80%. Although the titanium atoms are shown in this figure, their position is below their corresponding hydroxyl oxygen.

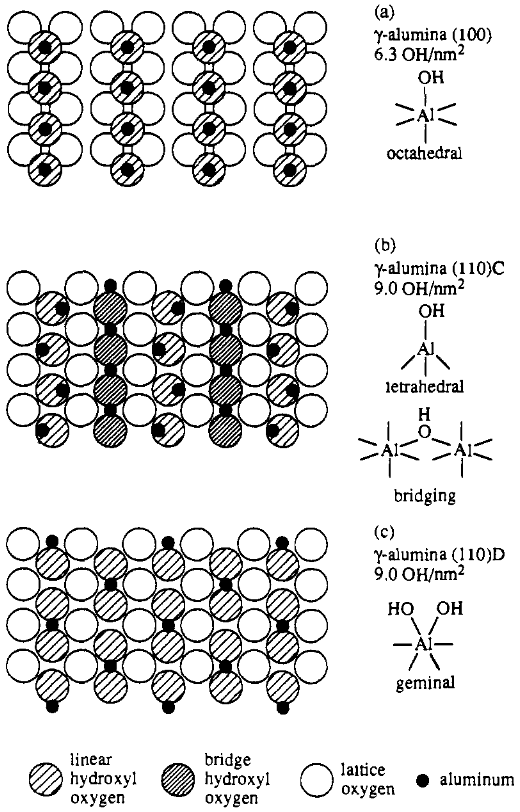

Figure 17. Representation of the surface structure of the fully hydroxylated (100), (110)C and (110)D planes of γ-alumina. The ionic radii of the atoms have been reduced to 80%. Although the aluminum atoms are shown in this figure, their position is below their corresponding hydroxyl oxygen.

Reaction of the silica surface with **1** at room temperature resulted in the formation of 1 equiv of propene. Heating this product to 50 °C yielded 0.5 equiv of propene. The reaction responsible for this evolution is difficult to characterize; however, it was likely the electrophilic cleavage of a second Rh–C bond by second hydroxyl group. The product of this may have been a mono-allyl rhodium complex covalently bonded to two oxygen atoms and possibly datively bonded to one oxygen atom as shown in surface complex V (Figure 10). It can be derived from surface complex I. There is no significant steric interaction between the allyl group and the surface. Figure 15 is a ball-and-stick representation of V, derived using CHEMX graphics.[38b]

Titania Support. Because of the ionic character of titania, molecular mechanics of this surface are less effective. Since Ti–O bonds are more ionic, the force fields are isotropic, and the structure is poorly described by the definition of bond lengths and angles. Another feature complicating the modeling of the titania surface is that the mechanism of dehydroxylation is not known. Thus the detailed molecular mechanics modeling used with silica is less likely to give useful results.

The EXAFS and high-resolution TEM studies of Martens et al.[27] indicated that the anatase phases of titania tended to expose preferentially the (001) and (101) faces. The structure of these two faces is illustrated in Figure 15. The (001) face has a square array of titanium atoms separated by 3.8 Å, and the (101) face has staggered rows of titanium atoms with a distance between the rows of 5.1 Å. This surface can also have hydroxyl groups coordinated to two titanium atoms. Complete hydroxylation of these surfaces results in 10.3 OH/nm^2 for the (101) and 7.0 OH/nm^2 for the (001); however, the studies of hydroxyl group concentrations on various oxide surfaces[22] indicate that titania pretreated at 200 °C has only 2.0 OH/nm^2. Dehydroxylation of these surfaces to the experimentally observed level of OH density results in an average (H)O···O(H) distance of 10 Å. Thus it is clear that formation of a bis-allyl rhodium complex by reaction with one OH and coordination with a neighboring one was much less likely on titania than silica. The species that formed on titania after reaction with a surface hydroxyl group could fill its 18-electron complement by coordination with an oxygen atom of the lattice,[14] since an OH was not available.

Alumina Support. Based upon the pseudomorphosis relations described by Lippens,[29,30] it was concluded that the preferentially exposed faces of γ-alumina are the (100) face and the C and D layers of the (110) planes.[31,32] The hydroxylated alumina surface was considered to be heterogeneous and has been described as being composed of local regions which are related to the (100), (110) C-layer, and (110) D-layers of hydroxylated γ-alumina. In summary, there are four different types of OH configurations: a terminal OH group coordinated to a single octahedral cation, a terminal OH group coordinated to a single tetrahedral cation, a bridging group which links two octahedral cations, and two terminal OH groups coordinated to the same octahedral cation. These three surfaces and their corresponding local structures are illustrated in Figure 16. Essentially the structure is a close-packed cubic lattice of oxygen anions with aluminum ions occupying various tetrahedrally and octahedrally coordinated sites. In this figure the ionic radii used to represent the atoms has been reduced to 80% for clarity. By comparison of our observed IR spectra of ν(OH) with those reported by others,[33] we tentatively assign our observed band at 3764 cm^{-1} to be the stretching vibration of an isolated OH bound to a single tetrahedral cation. The other two bands are assigned to OH groups that are involved in hydrogen bonds.

The study by Peri[28] indicates that pretreatment of alumina at 200 °C does not result in the loss of any of the OH groups on the surface. In fact, pretreatment at this temperature does not remove all of the water associated with the surface. Only pretreatment to higher temperatures results in activation of the surface. The reactivity of tris-allyl rhodium also follows this trend. No reaction was observed between **1** and alumina$_{(200)}$, while the formation of propene was observed when alumina$_{(350)}$ was exposed to **1**. This inactivity could be due either to the coordination of the surface hydroxyl groups to molecular water, thus making them inaccessible to the tris-allyl rhodium complex, or increasing the ionic character of the surface by removing hydroxyl groups.[31]

Discussion

The observed reactivity of the mineral oxides studied in this work with **1** followed the order: $TiO_{2(25-250)} > SiO_{2(25-550)} > Al_2O_{3(200-400)} \gg Al_2O_{3(25-200)} > MgO_{(200-400)}$. The action of **1** on the hydroxyl groups of titania leads to their immediate and total disappearance. With silica, the reaction took place more slowly, and it was possible to observe the decrease in the number of free silanol groups as a function of time. With alumina$_{(25-200)}$ no reaction of **1** was observed, while with alumina$_{(250-400)}$ a reaction occurred. With magnesia$_{(200-400)}$ only a very slow nonselective decomposition of **1** was observed. In general, the order of reactivity observed with these various oxides followed the order of pK_a values observed for the surface OH groups of these oxides [pK_a: TiO_2 (2 to 0.5) > SiO_2 (7.0) > Al_2O (8.5) ≫ MgO (18.5)].[22] The order of the pK_a values likely reflects the same ranking as the ranking of the electrophilic character of hydroxyl groups of the surfaces, and thus lends support to the hypothesis that electrophillic attack by surface hydroxyl groups is responsible for the observed reaction.

When tris-allyl rhodium reacted with these mineral oxides, only 1 equiv of propene was produced, and thus a bis-allyl rhodium moiety was likely grafted to the surface. The fact that, at room temperature, only one allyl group was eliminated, can be explained by a difference in the reactivity of one of the three allyl groups in the rhodium complex.[34] ^{1}H NMR studies[35] and X-ray determination[34] indicate a static trigonal prismatic structure in which the allyl groups in $M(\eta^3\text{-}C_3H_5)_3$ (M = Co, Rh) have two different arrangements. There is a unique axial allyl and two basal allyl groups. With both cobalt and rhodium complexes, only cleavage of the axial allyl group occurs during protolysis. For example, the reaction of hydrogen halide with tris-allyl rhodium produces a bis-allyl rhodium(III) derivative $[RhCl(\eta^3\text{-allyl})_2]_2$ and evolution of 1 equiv of propene. In contrast, treatment of these complexes with Lewis bases results in reductive elimination of the basal allyl groups to produce mono-allyl complexes with evolution of hexadiene.[34] In this case a $\eta^3 \leftrightarrow \eta^1$ interconversion is required before the elimination of the diene. When **1** was sublimed on the silica surface, chemisorbed and physisorbed species were indicated in the vibrational spectrum, Figure 3, but no characteristic vibrations of η^1-allyl at ca. 1640 cm^{-1} were observed. Thus since there was no spectroscopic evidence for an η^1 species and since no diene was observed, the reaction between **1** and the surface was likely an electrophilic attack of the surface hydroxyl groups on the complex and only one allyl group was eliminated. Although the mechanism was not identified, the protonation could occur either at metal center due to a high residual partial charge[36] or on the ligand due to the strong allyl character of the highest occupied molecular orbital.[37]

In the case of silica, the IR spectra of the reaction products contain a sharp band at 3636 cm^{-1} and a broad band at 3650 cm^{-1}, both of which have been attributed to the Si–OH–Rh bond. Note that the model complex $[Rh(\mu\text{-}OH)(\eta^3\text{-}C_3H_5)_2]$[25] possesses two ν(OH) vibrations situated at 3580 and 3549 cm^{-1}. Thus a hypothetical structure derived from this model has been proposed to exist on the surface. Modeling of the bis-allyl rhodium showed that this structure is reasonable since Rh–O distances of 2.20 Å can be set without significant close contact between the allyl group with surface atoms or significant deformation of the silica lattice.

Our results agreed with the stoichiometry described by reaction 1. In addition, it appeared that the coordination sphere of rhodium

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can reach an 18-electron configuration. The contradictory conclusions of Foley et al.[10] can be explained by considering the thermal stability of **2**. Our results of the thermal decomposition of **2** suggested that the two allylic ligands were not eliminated simultaneously. The results shown in Table IV indicated a significant evolution of propene (ca. 0.5 equiv/Rh at) between 40 and 100 °C. We suggested, therefore, that some **2** reacted via an "intramolecular" electrophilic attack of a coordinated OH group on an allyl ligand to liberate propene, giving a mono-allyl rhodium surface complex. In **2** the rhodium(III) atom could be coordinated to three surface oxygen atoms giving an 18-electron species.

On titanium dioxide dehydroxylated at a temperature below 250 °C, the formation of the bis-allyl rhodium complex was observed. In this case, the disappearance of the hydroxyl groups exhibiting vibrational bands at 3730 and 3680 cm^{-1} was always complete, whatever the degree of dehydroxylation of titanium dioxide. The amount of rhodium never exceeded 1.5% for dehydroxylation temperatures between 25 and 250 °C. To reach a stable 18-electron species, an oxygen atom of the crystalline network Ti–O–Ti may coordinate with the rhodium instead of hydroxyl group as in silica. This proposed structure requires further studies such as EXAFS and molecular modeling. Nevertheless, our results clearly indicated that on titania a bis-allyl surface fragment was obtained at room temperature and not a mono-allylic fragment as suggested from TPD experiments.[11]

The reaction of **1** with partially dehydroxylated alumina produced a bis-allyl rhodium species. The hydroxyl groups of alumina exhibiting vibrations at 3764, 3724, and 3680 cm^{-1} slowly disappeared during the reaction. The percentage of rhodium rarely exceeded 1% for the $alumina_{(250-400)}$. An alumina dehydroxylated below 200 °C did not react with **1**. This inactivity may be due to the coordination of the surface hydroxyl groups with molecular water. The appearance of vibrational bands characteristic of OH hydroxyl groups coordinated to the rhodium allyl, 3600–3650 cm^{-1}, was not observed after the reaction with alumina.

The adsorption of **1** on a $magnesia_{(200-400)}$ did not lead to reaction, and no new products were identified.

Conclusion

In summary, the interaction of $Rh(\eta^3\text{-}C_3H_5)_3$, **1**, with oxide supports gave results that vary according to the nature of the support and its degree of hydroxylation. With magnesia which has highly nucleophilic hydroxyl groups, as well as fully hydroxylated $alumina_{(25-200)}$, **1** did not react. With silica, titania, and partially dehydroxylated $alumina_{(200-500)}$, **1** reacted rapidly at room temperature, leading to the formation of a bis-allyl rhodium complex and a molecule of propene by the general reaction:

$$\gg M\text{–}O\text{–}H + Rh(\eta^3\text{-}C_3H_5)_3 \rightarrow \gg M\text{–}O\text{–}Rh(\eta^3\text{-}C_3H_5)_2 + C_3H_6 \tag{4}$$

$$M = Si, Ti, Al$$

Detailed spectroscopic studies based on labeling experiments (with ^{16}O–H, ^{18}O–H) and structural modeling lead us to suggest structures for the allylic species on the various supports. On silica two species seem to be present on the surface: one in which the rhodium is coordinated both to an oxygen and an OH coordinated to the same silicon atom and another in which the oxygen atom and the OH groups are coordinated to two different silicon atoms. Thermal treatment of the bis-allyl rhodium species above ca. 80 °C likely resulted in the reaction of some of the surface complexes to produce mono-allyl complexes, in which the rhodium was coordinated to two surface oxygen atoms. This complex could achieve an 18-electron count by bonding to a siloxane bridge oxygen:

$$(\gg Si\text{–})_2O + \gg SiO\text{–}H + \gg SiO\text{–}Rh(\eta^3\text{-}C_3H_5)_2 \rightarrow ((\gg Si\text{–})_2O)(\gg SiO\text{–})_2Rh(\eta^3\text{-}C_3H_5) + C_3H_6 \tag{5}$$

On titanium dioxide and alumina, the presence of OH groups coordinated to rhodium was not indicated in the FTIR spectra, but the rhodium complex could form an 18-electron species by coordination with other oxygen atoms of the surface.

Experimental Section

$Rh(\eta^3\text{-}C_3H_5)_3$ (**1**) was synthesized using the method described in the literature.[3,5] The FTIR spectra were recorded with a Nicolet-MX spectrometer.

Supports. Two types of silica were used for the infrared and quantitative studies: Degussa Aerosil ™200 and Shell S980 B1.5. Degussa Aerosil ™200 silica had a specific surface area of 200 m^2/g. To prepare the pellets, the silica was compressed (100 kg/cm^2), then ground in an agate mortar. Shell S980 B1.5 silica was manufactured as spheres having a diameter of 1.5 mm. The porous volume of this silica was 1.3 cm^3/g, and the surface area was 350 m^2/g. The pores had a diameter of 20 nm and allowed easy access for most products. A calcination at 400 °C under oxygen eliminated any organic residues.

The titanium dioxide used in our study was Degussa P 25™. It had a low specific surface, estimated to be 50 m^2/g. X-ray data indicate that it was ca. 80% anatase and 20% rutile.

Two types of alumina were used in this study. The Degussa C™ alumina had a low specific surface, 100 m^2/g. Since it was very finely divided, it was compressed (100 kg/cm^2) and then ground in an agate mortar. Rhone-Poulenc GFS C 200 alumina, pressed as 2-mm thick pellets was also used. This alumina had a surface of 230 m^2/g.

The magnesia used was prepared by dehydration of magnesium hydroxide. The specific surface was 100 m^2/g. The magnesium hydroxide was prepared by reaction of $MgCl_2$ with KOH in aqueous solution. The hydroxide was then washed with water and dried at 300 °C under vacuum. The percentage of chloride ions was less than 0.1%.

Gas. Argon (U, Air Liquide) was deoxygenated by passing over a deoxo-catalyst (BASF R-3-11). The deuterium used (N 20, Air Liquide) contained less than 1% hydrogen. Both gases were stored over molecular sieves (5 Å).

Adsorption Techniques. (a) Pretreatment of Supports. Before sublimation of **1**, the oxides were treated by slow heating in air to 400 °C. The surface was then alternately treated under oxygen (4 h) and under vacuum (10^{-5} Torr, 20 min) several times to degas the support, eliminate molecular water and carbonates present (on Al_2O_3, MgO), and oxidize the adsorbed hydrocarbons. The oxides were then rehydrated by contact with water vapor at 25 °C (pressure 22 Torr, 4 h). Then the oxides were placed under vacuum (10^{-5} Torr) for 16 h at a temperature between a minimum of 25 °C and a maximum of 550 °C. This method allowed the reproducible control of the concentration of water and hydroxyl groups on the surface of the oxides.

(b) Deposit of 1 by Sublimation. During the IR studies, **1** was first introduced into the tube which had been degassed and placed under argon. This tube containing **1** was then degassed under vacuum with liquid nitrogen and isolated by sealing with a torch. This tube was fixed to the IR cell.[13]

During the quantitative studies of the evolution of the products, qualitative analysis of the gas phase was carried out in standard volumetric equipment connected to a mass spectrometer. By this technique it was possible to determine with a high accuracy the nature of any evolved gas (CO, CO_2, H_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_6, C_4H_8, ...). Quantitative analysis was performed on several chromatographs. The products (CO, CO_2, CH_4, C_2H_4, and C_2H_6) were separated on a Porapak (R) column at 50 °C (H_2 gas vector). A methanation oven (Ni/MgO, 350 °C) was inserted between the column and the flame ionization detector which transformed CO and CO_2 into CH_4 in the presence of H_2 gas carrier. The CH_4 produced was thus analyzed. The hydrogen was analyzed by chromatography with a catharometer (Intersmat, IGC 120 MB) equipped with a molecular sieve column at 60 °C (argon carrier gas). A standard mixture (Air Liquide) was used to calibrate these two chromatographs.

(c) Molecular Modeling. The molecular modeling was performed with the CHEMX graphics system, and the molecular mechanics optimization was performed with Macro Model.[39] The ball-and-stick representations in the Figures 12–15 were drawn using the CHEMX modeling system developed by Chemical Design.[39] The ball-and-stick representation of the dirhodium complex was generated using the SYBYL modeling system developed by TRIPOS Associates.[40]

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(39) Created by E. K. Davies, Chemical Laboratory, Oxford University, and distributed by Chemical Design Ltd., Oxford, England.

(40) Created and distributed by TRIPOS Associates, St. Louis, MO.