Inorg. Chem. **1996,** *35,* 869−875 **869**

Surface Organometallic Chemistry on Oxides: Reaction of Trimethylphosphine with Bis(allyl)rhodium Grafted onto Silica

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Received May 23, 1994⊗

The reaction of $\mathrm{Rh}(\eta^3\text{-}\mathrm{C_3H_5})_3$ with the surface hydroxyl groups of partially dehydroxylated silica leads to the formation of the surface organometallic complex $(\equiv\mathrm{SiO})(\equiv\mathrm{SiOX})\mathrm{Rh}(\eta^3\text{-}\mathrm{C_3H_5})_2$, **1** (where X is H or Si≡), with evolution of propene. The reaction of **1** with $\mathrm{PMe_3}$ was examined, and two major pathways were discovered. Reductive elimination of two allyl ligands as 1,5-hexadiene and coordination of $\mathrm{PMe_3}$ give the surface product $(\equiv\mathrm{SiO})\mathrm{Rh}(\mathrm{PMe_3})_3$, **2**, which was characterized by elemental analysis, IR and ^{31}P MAS NMR spectroscopy. We also prepared **2** independently from $\mathrm{CH_3Rh(PMe_3)_3}$ and partially dehydroxylated silica. The second major reaction pathway is the elimination of propene to give $(\equiv\mathrm{SiO})_2\mathrm{Rh}(\eta^1\text{-}\mathrm{C_3H_5})(\mathrm{PMe_3})_3$, **3**. The presence of the σ-bound allyl ligand was inferred from its characteristic IR spectrum. The reactivity of **3** toward CO was examined: insertion of CO into the Rh−C bond followed by reductive elimination of the silyl ester $\equiv\mathrm{SiOC(O)C_3H_5}$ produces $(\equiv\mathrm{SiO})\mathrm{Rh(CO)(PMe_3)_2}$, **4**. In static vacuum, **3** decomposes to give allyl alcohol, which is slowly decarbonylated by **2**.

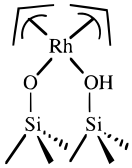
Introduction

Hydroxyl groups present on oxide surfaces are likely to play a role in the chemistry of oxide-supported metal catalysts. Our investigations of the surface organometallic chemistry of rhodium have revealed two possible reaction pathways. When rhodium contains no hydroxyl groups in its coordination sphere, its reaction chemistry is strictly comparable to that of molecular analogues. However, surface hydroxyl group(s) are coordinated to some surface organometallic rhodium fragments, and may participate in the reactions. In the latter case, molecular chemistry does not adequately model the surface reactivity.

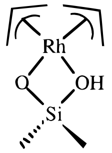
The well-defined bis(allyl)rhodium surface complex is our starting point, since the coordination sphere of the surface organometallic fragment is well-defined. It is prepared on partially dehydroxylated silica according to the reaction stoichoimetry shown in eq 1.[1,2] The direct coordination of the

$$\equiv\mathrm{Si\text{-}OH} + \mathrm{Rh}(\eta^3\text{-}\mathrm{C_3H_5})_3 \rightarrow \underset{\mathbf{1}}{(\equiv\mathrm{SiO})\mathrm{Rh}(\eta^3\text{-}\mathrm{C_3H_5})_2} + \mathrm{C_3H_6} \tag{1}$$

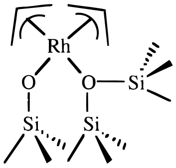
rhodium to a surface oxygen atom has been observed by Raman spectroscopy[1] and, on the titania surface, by EXAFS.[3] Three microenvironments have been proposed for **1** on the silica surface, based on molecular analogies,[4] IR evidence[2] and theoretical calculations.[5] A sharp IR band at 3636 cm^{-1} was assigned to the ν(OH) vibration of a rigid silanol group perturbed by coordination to Rh (species **1b**), Table 1, whereas a broad IR band in the same region was ascribed to a less rigid coordinated silanol such as in **1a**.[2]



1a



1b



1c

We have found that the surface chemistry of **1** is strongly influenced by the presence and quantity of surface hydroxyl groups.[6] Silanol groups were also found to be essential for the reductive carbonylation of silica-supported $\mathrm{RhCl_3}$ to $[\mathrm{Rh(CO)_2Cl}]_2$ and $\mathrm{Rh_6(CO)_{16}}$.[7] These processes require surface mobility of the organometallic fragments, which is favored by the presence of silanols. The extent of nucleation appears to depend directly on the surface water content.[8] The subject of this report is the reaction of **1** with $\mathrm{PMe_3}$, which affords two different silica-supported phosphine complexes of Rh, whose relative amounts depend on the silanol content of the silica.

Results

Adsorption of $\mathrm{PMe_3}$ on Silica. The addition of $\mathrm{PMe_3}$ (100 Torr) to silica$_{300}$[9] causes the nearly complete disappearance of the free silanol groups (≡Si-OH) as judged by the decrease in intensity of the band at 3747 cm^{-1}. At the same time, a broad band attributed to hydrogen-bonded silanols appears at 3300 cm^{-1}. The solid-state proton-decoupled ^{31}P MAS spectra of this material gave a sharp resonance at −61.3 ppm (liquid-like

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

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(9) The notation silica$_{300}$ means that silica was dehydroxylated under dynamic vacuum at 300 °C.

Table 1. Identification of Surface Species and Comparison with Molecular Analogues

compound		infrared bands		elem anal. P/Rh	^{31}P chem shift, δ (ppm)	ref
formula	no.	frequency (cm^{-1})	assignment			
$(\equiv SiO)(\equiv SiOH)Rh(\eta^3\text{-}C_3H_5)_2$	**1**	3636	ν(O−H)			2
		3048, 2992	ν(C−H)			
		1492, 1462	$\delta(CH_2)$			
		1391	ν(C−C−C)			
$(\equiv SiO)Rh(PMe_3)_3$	**2**	2967, 2906	ν(C−H)	3.1	−2.5, −10.6	this work
		1422, 1295	$\delta(CH_3)$			
$ClRh(PMe_3)_3$		2980, 2900	ν(C−H)		−0.38 (td), −11.31 (dd)[a]	16
		1435, 1425, 1290	$\delta(CH_3)$			
$CH_3Rh(PMe_3)_3$					6.80 (d), −20.2 (br m)	
$(\equiv SiO)_2Rh(\eta^1\text{-}C_3H_5)(PMe_3)_3$	**3**	3072	ν(=C−H)			
		2967, 2905	ν(C−H)	3.1	−13.2, 24.3	this work
		1612	ν(C=C)			
		1422, 1295	$\delta(CH_3)$			
$(\equiv SiO)Rh(CO)(PMe_3)_2$	**4**	2974, 2908	ν(C−H)	1.9	−9.3	this work
		1975	ν(CO)			
		1422, 1295	$\delta(CH_3)$			
$ClRh(CO)(PMe_3)_2$		2970, 2910	ν(C−H)			
		1960	ν(CO)		−10.22 (d)[b]	16
		1425, 1420, 1275	$\delta(CH_3)$			
$\equiv SiOC(O)CH_2CH{=}CH_2$	**5**	3072	ν(=C−H)			6
		1765	ν(CO)			
		1643	ν(C=C)			

[a] In toluene-d_8. [b] In C_6H_6−C_6D_6 (10%).

PMe_3) and a very weak, broad resonance at 43.6 ppm (adsorbed $O{=}PMe_3$).[10] The free silanol groups are completely regenerated by evacuation of the IR cell at room temperature. This result was confirmed by volumetric adsorption and desorption measurements: PMe_3 which is adsorbed on silica$_{300}$ is recovered quantitatively by desorption to a liquid N_2 trap. Thus PMe_3 is reversibly adsorbed on partially dehydroxylated silica. This finding is consistent with previous studies.[11]

Reaction of $(\equiv SiO)Rh(\eta^3\text{-}C_3H_5)_2$, 1, with PMe_3. The formation of **1** by the reaction of $Rh(\eta^3\text{-}C_3H_5)_3$ with partially dehydroxylated silica (pretreated at 200−550 °C) has been described in detail.[1,2,12] One equivalent of propene per chemisorbed Rh is evolved, giving a yellow supported complex with two allyl ligands bound to Rh, eq 1. It has also been shown that when the reaction takes place on deuterated silica, the gaseous product is exclusively propene-d_1.[13] The IR spectrum of **1**, Figure 1, contains bands at 1492, 1462, and 1391 cm^{-1} characteristic of allyl ligands coordinated in an η^3-fashion.

Qualitative and Quantitative Analysis. The reaction of **1** with 0.1 Torr of PMe_3 caused the sample to change color from dark yellow to light yellow. 1,5-Hexadiene and propene were liberated into the gas phase, and were identified by GC. The relative amounts of the two gaseous products depend on the degree of dehydroxylation of the silica, Table 2. On silica dehydroxylated at ≥400 °C, both gaseous products were observed. On silica dehydroxylated at <400 °C, propene was almost exclusively observed. The reaction of **1** with PMe_3 was also performed on partially deuterated silica. The degree of deuteration (26 ± 2%, by exchange of ≡SiOH with D_2O) was determined by the ratio of propene-d_1 to propene-d_0 released during the grafting of $Rh(\eta^3\text{-}C_3H_5)_3$ (see above). The propene liberated by the reaction with PMe_3 contained 22 ± 2% propene-d_1. Elemental analysis of the solid product gave the ratio P/Rh = 3.1 ± 0.5 (average of eight separate experiments) and 13.6 ± 0.7 C/Rh (average of five separate experiments), regardless of the degree of dehydroxylation of the silica. Allyl alcohol was extracted from the surface with H_2O and detected by GC.

Table 2. Qualitative and Quantitative Analysis of Gases Evolved During the Reaction of $(\equiv SiO)(\equiv SiOX)Rh(\eta^3\text{-}C_3H_5)_2$, **1** (where X is H or Si≡), with PMe_3

surface	Rh/mmol	gas	quantity/mmol	C_3 equiv
silica$_{400}$	0.139	propene	0.111	0.80
		1,5-hexadiene	0.026	0.37
				tot. 1.17
silica$_{300}$	0.173	propene	0.146	0.85
		1,5-hexadiene	0.002	0.01
				tot. 0.86

IR Spectroscopy. Upon addition of PMe_3 to **1** followed by evacuation to desorb excess phosphine, the characteristic vibrations of the η^3-C_3H_5 ligands ($\delta(CH_2)$ 1492, 1462 cm^{-1}; ν(C−C−C) 1391 cm^{-1}, Table 1) disappeared. The peak due to free silanols at 3747 cm^{-1} also disappeared as well as the sharp ν(OH) band at 3636 cm^{-1} assigned to a silanol coordinated to rhodium (structure **1b**).[2] New bands appeared at 2967, 2905, 1422, and 1295 cm^{-1}, assigned to the ν(C−H) and $\delta(CH_3)$ modes of PMe_3 which is strongly bound on the surface (not desorbed under dynamic vacuum), in contrast to the behavior of PMe_3 on silica. In addition, new bands not attributable to PMe_3 appeared at 3072 and 1612 cm^{-1}, Figure 2.

The new IR bands described above are stable under dynamic vacuum (10^{-5} Torr, 1 h). However, prolonged dynamic vacuum (48 h) led to a slight decrease (ca. 15%) in the absorbance of the phosphine bands and the ultimate disappearance of the bands at 3072 and 1612 cm^{-1}. The latter were not regenerated when additional PMe_3 was reintroduced. At the same time, an intense band at 1960 cm^{-1} appeared. The species responsible for this band does not react with H_2O or with CH_3I.

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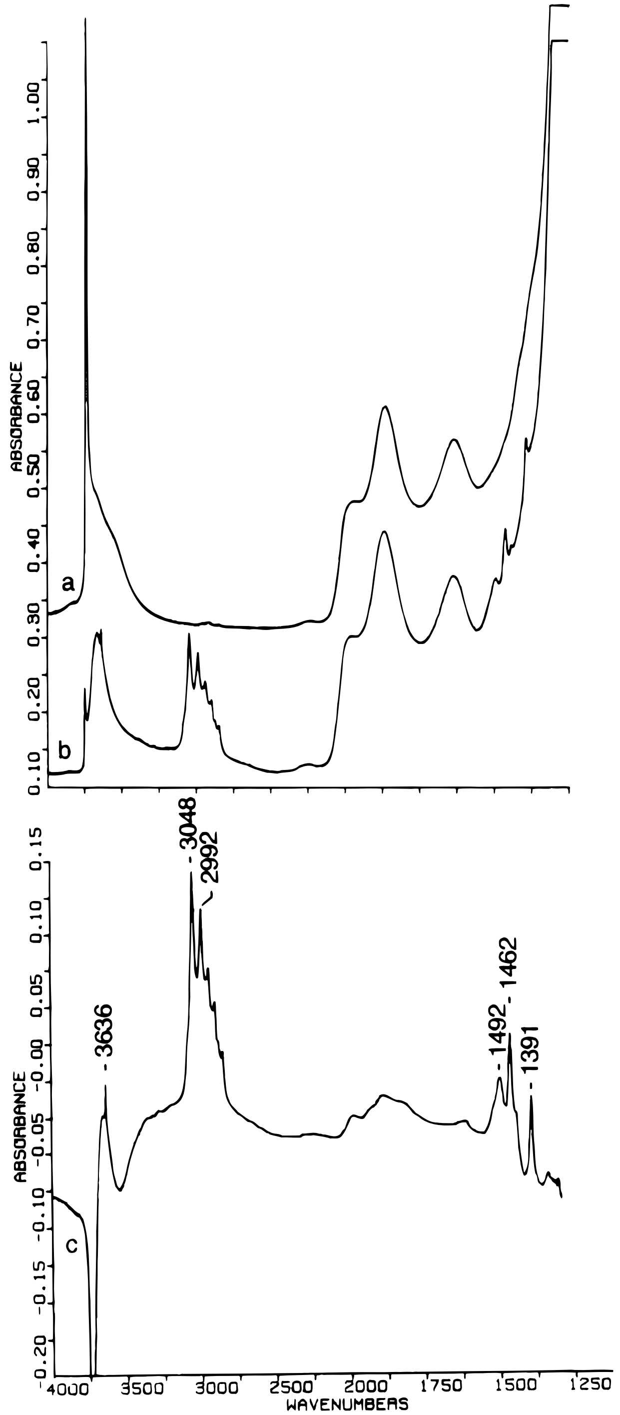

Figure 1. (a) IR spectrum of silica$_{400}$. (b) IR spectrum of (≡SiO)(≡SiOX)Rh(η^3-C_3H_5)$_2$, **1** (X is H or Si≡) on silica$_{400}$. (c) Difference spectrum: spectrum b − spectrum a.

Reactivity. Reaction with CO. The product of the reaction of $\mathbf{1}_{400}$ with PMe_3 was exposed to 100 Torr of CO. After evacuation of the excess CO, the IR peaks at 2967 and 2905 cm^{-1} due to the phosphine ligands had decreased in intensity by ca. 33%. The band at 1960 cm^{-1} increased dramatically in intensity, and a new band appeared at 1765 cm^{-1}, Figure 3. The latter two bands were stable under dynamic vacuum and under H_2. Elemental analysis of the solid yielded 1.9 P/Rh.

Reaction with H$_2$. The addition of 100 Torr of H_2 to the product of the reaction of **1** with PMe_3 caused no change in the color of the solid. However, after 48 h at room temperature, the gas phase contained propene (major) and propane (minor), observed by IR and GC. The IR bands at 3072 and 1612 cm^{-1} disappeared slowly on the same time scale.

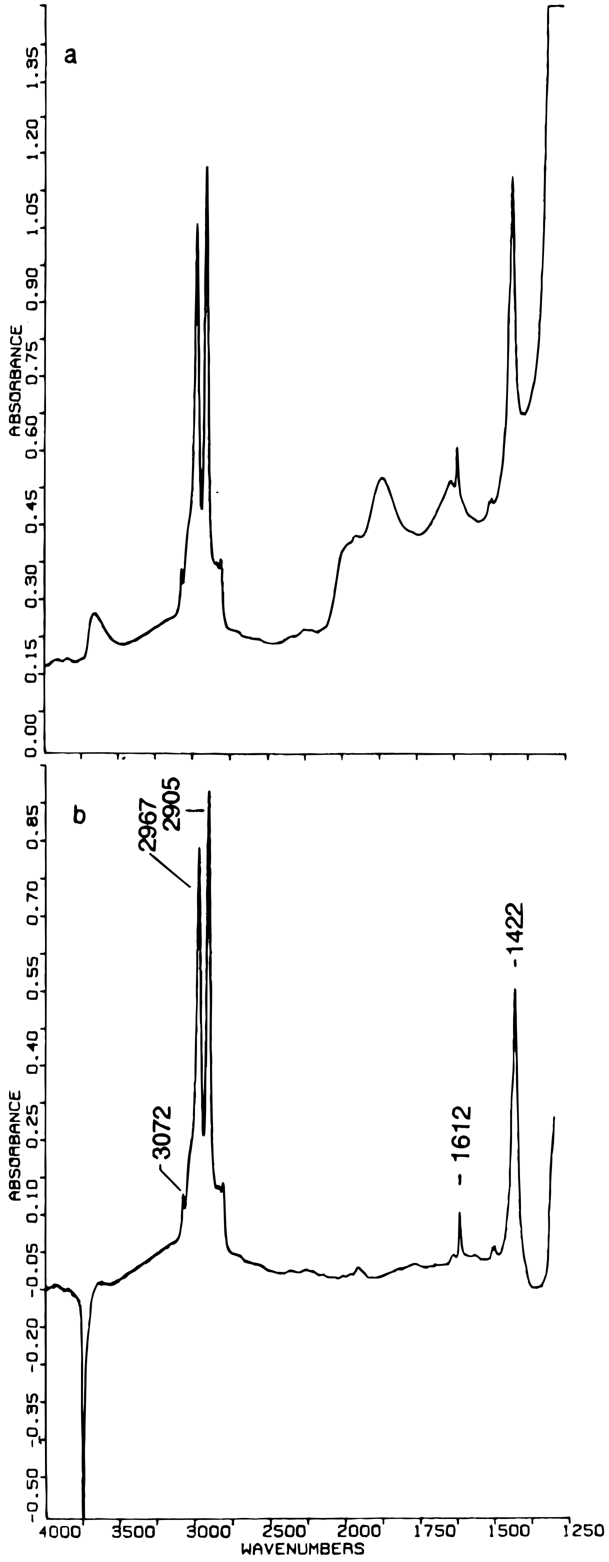

Figure 2. (a) IR spectrum of the products ≡SiORh(PMe_3)$_3$, **2**, and (≡SiO)$_2$Rh(η^1-C_3H_5)(PMe_3)$_3$, **3**, obtained by the reaction of **1** with excess PMe_3, followed by evacuation of the sample. (b) Difference spectrum from spectrum a obtained by subtraction of the background spectrum of silica$_{400}$.

Solid-State ^{31}P MAS NMR. The material obtained by the reaction of **1** with PMe_3 was studied by proton-decoupled ^{31}P MAS NMR, Figure 4. The spectrum of a fresh sample on silica$_{200}$ contains two major resonances at −2.5 and −10.6 ppm, with line widths of 310 and 608 Hz, respectively, and a small band at −24.8 ppm, Figure 4a. The areas of the two major resonances are in the ratio of 1:1.6. The spectrum of an aged

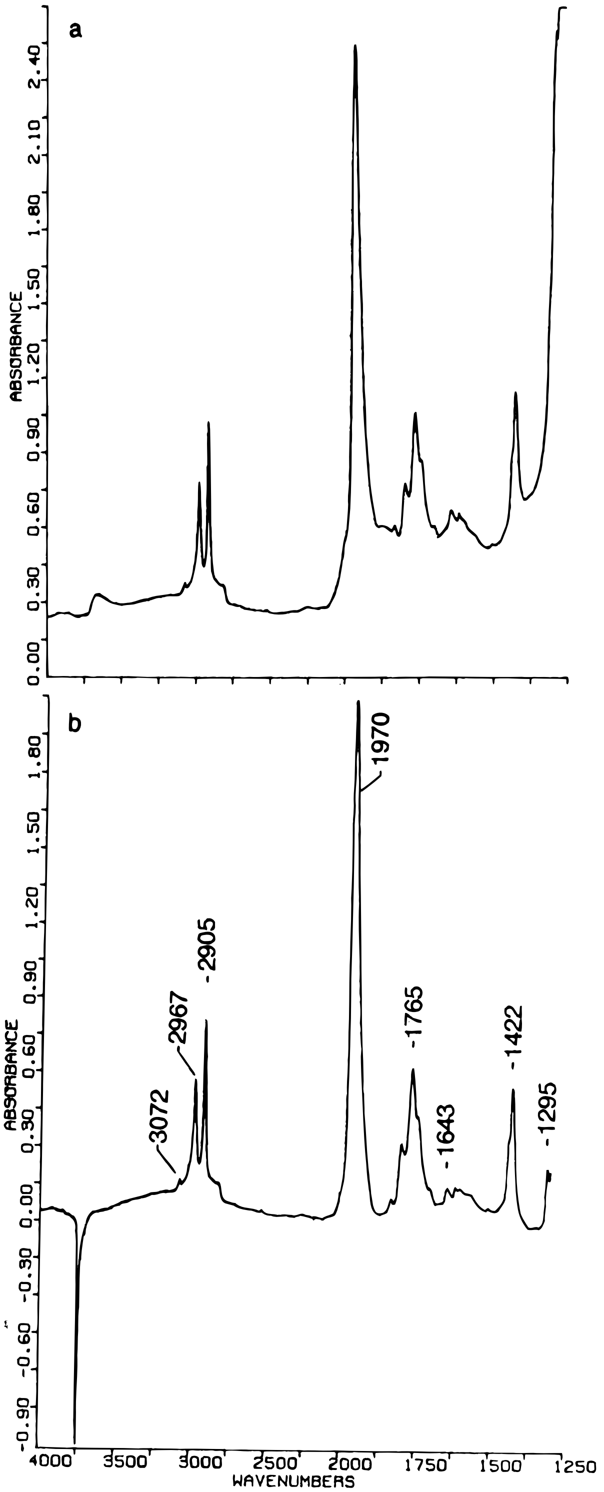

Figure 3. (a) IR spectrum of ($\equiv$SiO)Rh(CO)(PMe$_3$)$_2$, obtained by the reaction of **1**$_{400}$ with PMe$_3$ followed by CO. (b) Difference spectrum from spectrum a obtained by subtracting the background spectrum of silica$_{400}$.

sample (several days at room temperature) on silica$_{200}$ contains a much broader band at ca. −13 ppm, Figure 4b. No coupling to P or Rh could not be resolved due to the large line widths of all the bands (coupling constants $J(^{103}\mathrm{Rh}-^{31}\mathrm{P})$ are generally in the range 80−120 Hz).[14] On silica$_{550}$, three resonances were observed at −2.0, −12.4, and −24.8 ppm, Figure 4c.

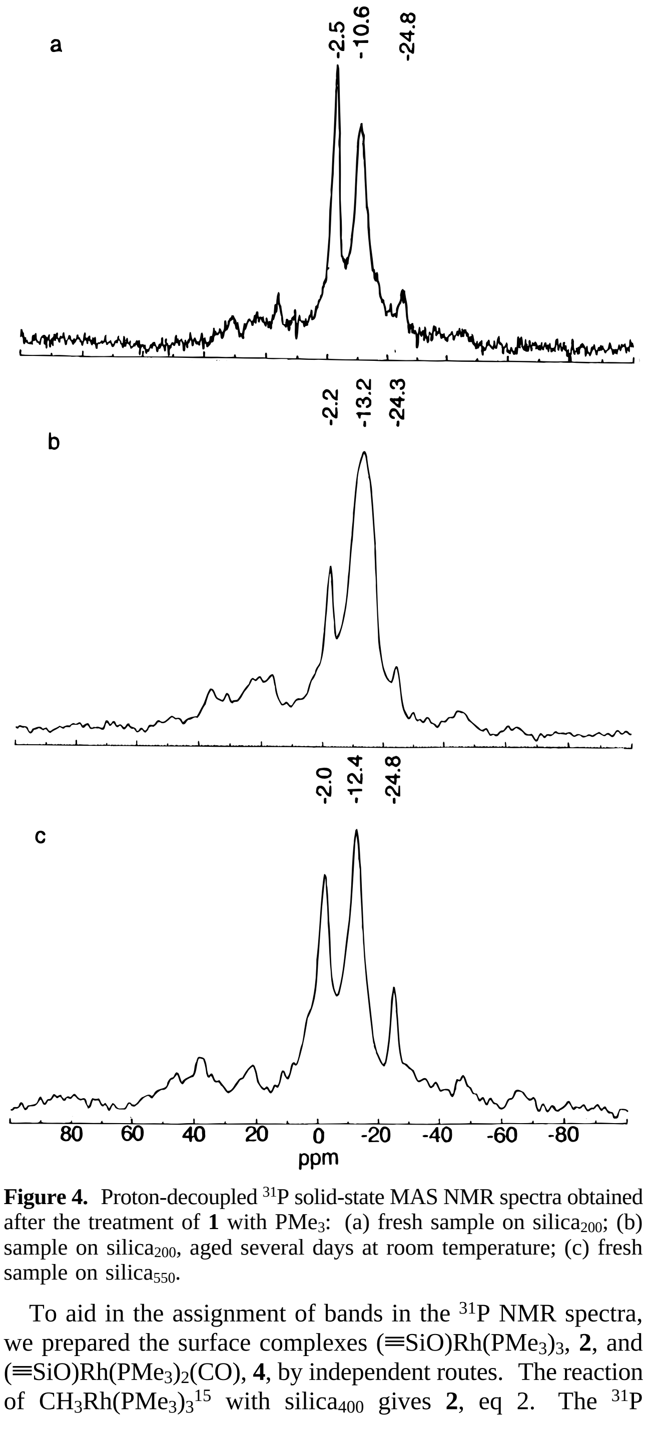

Figure 4. Proton-decoupled ^{31}P solid-state MAS NMR spectra obtained after the treatment of **1** with PMe$_3$: (a) fresh sample on silica$_{200}$; (b) sample on silica$_{200}$, aged several days at room temperature; (c) fresh sample on silica$_{550}$.

To aid in the assignment of bands in the ^{31}P NMR spectra, we prepared the surface complexes ($\equiv$SiO)Rh(PMe$_3$)$_3$, **2**, and ($\equiv$SiO)Rh(PMe$_3$)$_2$(CO), **4**, by independent routes. The reaction of CH$_3$Rh(PMe$_3$)$_3$[15] with silica$_{400}$ gives **2**, eq 2. The ^{31}P

$$\mathrm{CH_3Rh(PM_3)_3 + {\equiv}SiOH \rightarrow \underset{\mathbf{2}}{({\equiv}SiO)Rh(PMe_3)_3} + CH_4} \qquad (2)$$

spectrum of **2** has two resonances at −1.4 and −12.0 ppm. These are assigned to cis and trans phosphine ligands, respectively, by comparison to the spectrum of the molecular complex ClRh(PMe$_3$)$_3$, −0.38 (cis) and −11.31 (trans) ppm.[16] Reaction of **2** with CO gave **4**, with a single resonance at −9.3 ppm.

Discussion

The formation of 1,5-hexadiene by the reaction of **1** with PMe$_3$ occurs only when **1** is supported on silica dehydroxylated

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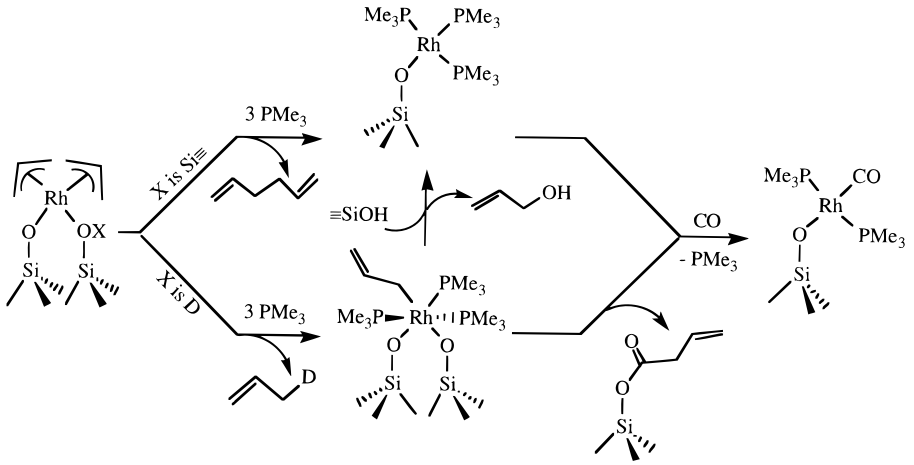
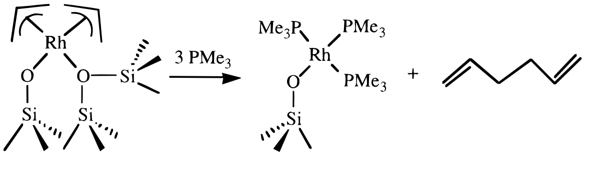
Scheme 1



at ≥400 °C. The 1,5-hexadiene is proposed to arise by reductive elimination of two allyl ligands from the coordination sphere of Rh, eq 3. A similar formation of 1,5-hexadiene was

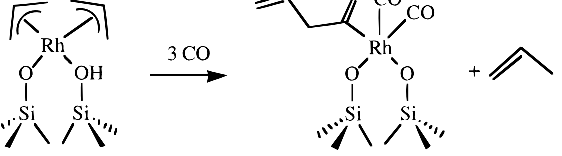


(3)

1c **2**

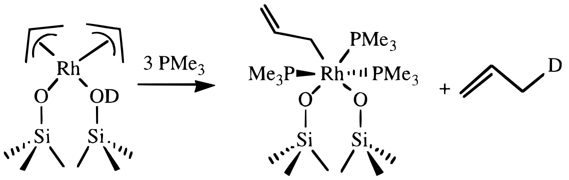
previously observed in the reaction of $\mathbf{1}_{400}$ with CO[6] and has precedent in the molecular chemistry of $[\mathrm{ICo}(\eta^3\text{-}C_3H_5)_2]_2$.[17] The product **2** contains 3P/Rh, consistent with the elemental analysis. The resonances at −2.5 and −10.6 ppm in the ^{31}P NMR spectrum of a fresh sample (Figure 4a) are attributed to **2**, Table 1, by comparison to an authentic sample of **2** prepared by the reaction of $CH_3Rh(PMe_3)_3$ with silica (see above). The areas of the two resonances are roughly consistent with the assignment of the −2.5 ppm resonance to the cis phosphorus and the −10.6 ppm resonance to the two trans phosphorus atoms. The observation that the latter resonance is roughly twice the line width of the former causes us to suggest that the trans phosphorus atoms do not have identical environments, which may be an effect of the surface. Reaction 3 is also consistent with the disappearance of IR bands due to η^3-C_3H_5 ligands of **1**. However, it does not explain the appearance of new bands at 3072 and 1612 cm^{-1}. The presence of an additional resonance at −24.8 ppm in the ^{31}P NMR spectrum also indicates a second reaction pathway leading to a second surface organometallic fragment.

The second gas phase product from the reaction of **1** with PMe_3 on silica$_{400}$ is propene, and this is the exclusive product on silica dehydroxylated at <400 °C. Propene was previously observed in the reaction of $\mathbf{1}_{200}$ with CO,[6] where it was proposed to originate in an electrophilic attack of a proton in or near the coordination sphere of Rh on one of the allyl ligands, eq 4.



(4)

The electrophilic cleavage of the rhodium−carbon bond by a surface silanol is apparently also induced by PMe_3. The proposed mechanism for propene formation is supported by the partial deuteration experiment. Thus, the amount of monodeuterated propene liberated by the reaction of **1** with PMe_3 corresponds to the amount of deuterium incorporated into surface silanol groups, eq 5. The elimination of propene and



(5)

1a **3-mer**

coordination of PMe_3 to Rh is accompanied by an $\eta^3 \rightarrow \eta^1$ shift of the second allyl ligand, eq 5. The IR bands at 3072 and 1612 cm^{-1} are characteristic of a σ-allyl group coordinated to a metal atom.[18] These bands are assigned to the ν(=C−H) and ν(C=C) modes, respectively, of **3**. The $\eta^3 \rightarrow \eta^1$ shift was inferred in the reaction of **1** with CO, eq 4; however, rapid insertion of CO into the Rh−C bond to give an acyl complex prevented the characterization of a σ-allyl complex comparable to **3**.[6] Because insertion is not a reaction pathway available to PMe_3, the σ-allylrhodium complex **3** was directly observed as the product of reaction 5. Note that **3** contains 3P/Rh, also consistent with the elemental analysis. Thus the ratio P/Rh does not distinguish between the products **2** and **3**. The two bands in the ^{31}P spectrum at −13.2 and −24.3 ppm are assigned to phosphine ligands of **3**.[15] In particular, we assign the −13.2 ppm resonance of **3** to P trans to a siloxy ligand and the highly shielded resonance at −24.3 ppm to P trans to P. On the basis of the assumption that the resonances at −2.0 and −24.8 ppm belong to the different surface species **2** and **3**, the ratio of **2**:**3** on silica$_{550}$ is approx. 3:1.

Additional evidence for the presence of the allyl ligand in complex **3** is the ready insertion of CO into the metal−carbon bond. The 3-butenoate ligand undergoes reductive elimination with a siloxy ligand to give a silyl ester, **5**, with ν(CO) and ν(C=C) modes at 1765 and 1643 cm^{-1}, respectively. We recently reported the formation of the silyl ester of 3-butenoate in the reaction of **1** with CO.[6] The silyl ester **5** is stable under dynamic vacuum and in the presence of H_2. Note that

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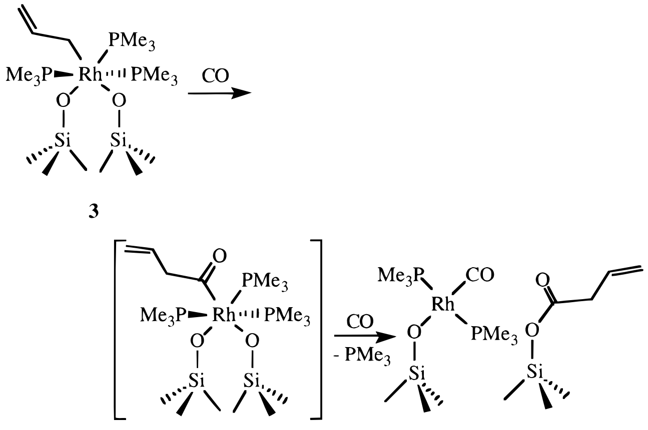
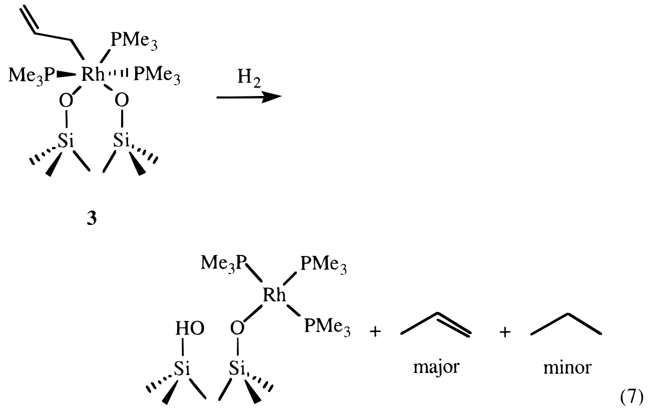


3

4 **5** (6)

acylrhodium complexes have much lower ν(CO) frequencies, e.g. 1708 cm^{-1} for $[Rh(COMe)Cl_2(PPh_3)_2]_2$,[19] and are highly susceptible to hydrogenolysis.[20] CO coordinated to Rh, as in **4**, gives rise to the band observed at 1960 cm^{-1}. For comparison, the molecular analogue *trans*-$ClRh(PMe_3)_2(CO)$ has ν(CO) at 1960 cm^{-1}.[16] The surface reactions are summarized in Scheme 1.

Under H_2, the IR bands due to the σ-allyl ligand disappear slowly, implying a reaction of **3** with H_2. The simultaneous increase in ν(OH) intensity in the IR spectrum suggests the following reaction:



3

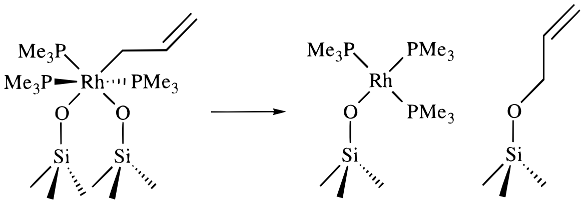
2

(7)

The allyl ligand is released into the gas phase primarily as propene.

On $silica_{200}$ as well as on $silica_{550}$, a mixture of two surface species was always obtained, i. e., **2** and **3**. This conclusion is based on the similarity of ^{31}P NMR spectra on $silica_{200}$ and $silica_{550}$, Figure 4. However, the surface reactions leading to **2** and **3**, eqs 3 and 5, lead to different gas phase products. Since 1,5-hexadiene is not formed during the reaction of $\mathbf{1}_{200}$ with PMe_3, Table 2, we anticipated that **3** would be the only Rh surface product in that reaction. However, the IR and NMR spectra both indicate that the surface of $silica_{200}$ contains the product **2** as well as **3**.

We propose that a portion of the initially-formed product, **3**, is transformed by a subsequent reaction into **2**. This process may be reductive elimination of the σ-allyl ligand with a siloxy ligand to give a surface ether, eq 8. Indeed, allyl alcohol was extracted from the surface and identified by GC. The presence of additional carbon on the surface after reaction with PMe_3 and even after hydrogenolysis of the allyl ligand of **3** (see below) is also revealed by the C/Rh ratio, 13.6 ± 0.7, which is significantly higher than expected from the 9C/Rh due to three PMe_3 ligands. Under prolonged dynamic vacuum, **3** is eventually completely transformed into **2** with loss of the allyl ligand, according to eq 8. The transformation of the silyl ether into allyl alcohol is possible in the presence of surface silanols.[21]



(8)

3 **2**

Additional evidence for the presence of allyl alcohol on the surface was found in the appearance of the band at 1960 cm^{-1} when the surface complexes (**2** + **3**) were stored under vacuum for several days. The decarbonylation of allyl alcohol by **2** gives rise to the rhodium carbonyl species **4**, eq 9, with ν(CO) at

$$\underset{\mathbf{2}}{(\equiv SiO)Rh(PMe_3)_3} + CH_2{=}CHCH_2OH \rightarrow \underset{\mathbf{4}}{(\equiv SiO)Rh(PMe_3)_2(CO)} + CH_3CH_3 + PMe_3 \quad (9)$$

1960 cm^{-1}. The analogous homogeneous decarbonylation of allylic alcohols by $ClRh(PPh_3)_3$ has been reported.[22] During the surface reaction, the IR bands of coordinated PMe_3 decreased in intensity by 33%, and the P/Rh ratio decreased from 3.1 to 1.9, consistent with the stoichiometry shown in eq 9.[23]

Conclusion

The reaction of **1** with PMe_3 depends strongly on the hydroxyl content of the silica surface. As in our previous study of the reaction of **1** with CO, the allyl ligands may be eliminated from the surface as either 1,5-hexadiene or propene. Two tris(trimethylphosphine) complexes of Rh are formed, one of which retains an η^1-allyl ligand. We report the first directly observed π → σ-allyl isomerization in a well-defined surface organometallic complex. The Rh−C σ-bond is apparently unstable and is slowly eliminated.

Experimental Section

General Data. The techniques of surface organometallic chemistry, in particular *in situ* experiments, have already been described.[2] They involve sublimation of $Rh(\eta^3\text{-}C_3H_5)_3$ 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. The use of break-seal techniques avoids any possible contamination of surface complexes by air.

Supports. The silica used for the infrared and volumetric studies was Degussa Aerosil 200, with a specific surface area of 200 m^2/g. The silica was compressed (100 kg/cm^2), ground in an agate mortar then treated by slow heating in air to 400 °C in an all-glass reactor. The surface was then treated alternately under oxygen (4 h) and under vacuum (10^{-5} Torr, 20 min) several times to degas the support,

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eliminate adsorbed molecular water, and oxidize adsorbed hydrocarbons. The silica was then rehydrated by contact with water vapor at 25 °C (22 Torr, 4 h) and then placed under vacuum (10^{-5} Torr, 16 h) at the desired temperature between 200 and 550 °C. This method allows reproducible control of the concentration of water and hydroxyl groups on the oxide surfaces.

Preparation of 1. $Rh(C_3H_5)_3$, synthesized as described in the literature,[24] 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 a glass reactor or an *in situ* IR cell. After preparation of the support, either as a powder or a self-supporting wafer (see above), the break-seal connecting the tube containing $Rh(allyl)_3$ and the reactor was broken. $Rh(C_3H_5)_3$ sublimed onto the support at room temperature under vacuum without exposure to air. Unreacted $Rh(C_3H_5)_3$ was removed from the surface with a liquid N_2 trap.

Reaction of 1 with PMe_3. The introduction of PMe_3 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. The gaseous products were separated on KCl/Al_2O_3 (hydrocarbons) or Carbowax (alcohols) columns isothermal at 70 °C. IR spectra were recorded on a FT-Nicolet 10-MX spectrophotometer. Similar procedures were used to introduce CO and H_2. Analysis for Rh, P, and C content was performed at the end of the experiment.

For NMR studies, samples were transferred to zirconia rotors in an argon-filled glovebag. ^{31}P MAS NMR spectra were obtained on a Bruker MSL-300 spectrometer operating at 121.4 MHz., using magic angle spinning (ca. 4 kHz) and proton-decoupling. A short pulse length was used (2 μs, corresponding to a rotation of ca. 30° of the magnetization), and spectra were acquired with high power proton decoupling. A delay of 2 s was used between each scan. It was checked that this was sufficient to allow for complete relaxation of the ^{31}P nuclei by recording spectra with various delays. Chemical shifts were referenced to 85% H_3PO_4. The error in the reported chemical shifts is approximately 0.3 ppm.

Acknowledgment. S.L.S. thanks NATO and the Ministère des Affaires Etrangères (France) for postdoctoral support. P.D. thanks the CNRS for a doctoral fellowship. We are very grateful to Dr. F. Lefebvre for recording the solid-state NMR spectra.

IC9405790

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