Ligand Exchange and Oxidative Addition on a Silica-Supported Rhodium Complex, *trans*-[($\equiv$SiO)Rh(PMe_3)$_2$(CO)]

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Abstract: The surface organometallic fragment [$Rh^I(P(CH_3)_3)_2(CO)$], **1**, was prepared by the reaction of *trans*-[$CH_3Rh(P(CH_3)_3)_2(CO)$] with partially dehydroxylated silica. **1** is attached to the silica surface by a covalent bond to oxygen. The reactions of **1** with organic and inorganic substrates were followed by transmission infrared and solid-state NMR spectroscopies. Ligand exchange reactions were observed when **1** was treated with ^{13}CO and $P(CH(CH_3)_2)_3$. In the presence of excess PR_3 (R is methyl or isopropyl), cationic [$Rh(PR_3)_3$-$CO]^+$ was formed. In the presence of HCl/DCl, Cl_2, CCl_3Br, CH_3I, and $CH_2{=}CHCH_2Cl$, **1** underwent oxidative addition to give Rh(III) surface species, characterized by a shift of the ν(CO) modes ca. 100 cm^{-1} to higher frequency and displacement of the ^{31}P chemical shifts to lower field. In the case of HCl/DCl, ν(Rh−H/D) modes were also observed. Oxidative addition of CH_3I to **1** occurs without CO insertion, but the formation of acyl complexes was induced by addition of excess $P(CH_3)_3$ or CO. The reaction of **1** with $CH_2{=}CHCH_2Cl$ exhibits biphasic kinetic behavior, implying consecutive elementary reactions of oxidative addition followed by spontaneous CO insertion into the metal−carbon bond. The demonstration of these reactions on an oxide surface supports the idea that, under carefully controlled conditions, surface reactivity can be interpreted by using concepts from organometallic chemistry.

Introduction

One of the most dramatic examples of adsorbate-induced restructuring of metal surfaces[1] is the reaction of CO with supported Rh metal particles. Crystallites of Rh, supported on silica or alumina, are completely disrupted by adsorption of CO,[2] leading to the formation of atomically dispersed mononuclear metal sites $Rh^I(CO)_2$ (on alumina)[3−6] and dinuclear sites [Rh^I-$(CO)_2]_2$ (on silica).[7,8] Like similar molecular complexes,[9] these surface organometallic fragments undergo photodissociation of CO to produce unsaturated species which react with alkane C−H bonds by oxidative addition.[10] However, despite the strong interaction of CO with Rh metal, $[Rh^I(CO)_2]_x$ ($x = 1$ or 2) is not stable under H_2. Upon exposure to H_2, Rh is reduced and aggregates to form CO-covered metal particles.[2,8]

Phosphines bind strongly to metal surfaces, displacing other ligands.[11,12] For example, phosphine was reported to react irreversibly with $Rh^I(CO)_2$ on alumina by displacing CO, to form $Rh^I(PH_3)(CO)$.[13] The coordination of electron-donating phosphines subsequently stabilizes the dispersed metal toward aggregation under H_2.[14] This phenomenon is well-documented in molecular chemistry, where many complexes of the type $XRh(PR_3)_3$ and $XRh(PR_3)_2(CO)$ have long been investigated for their catalytic activity in hydrogenation[15] and hydroformylation[16] and, more recently, in C−H activation and functionalization.[17−19] The ability of the 16e$^-$ Rh(I) complex to coordinate small molecules and undergo oxidative addition is generally considered to be the key to its catalytic activity. Surface analogues of these complexes were reported in the reaction of [$\equiv$SiORh(η^3-C_3H_5)]$_2$ with CO, followed by partial displacement of CO by $P(CH_3)_3$.[14] In this study, we report the preparation of a stable rhodium surface complex with both carbonyl and phosphine ligands. Its characterization is facili-

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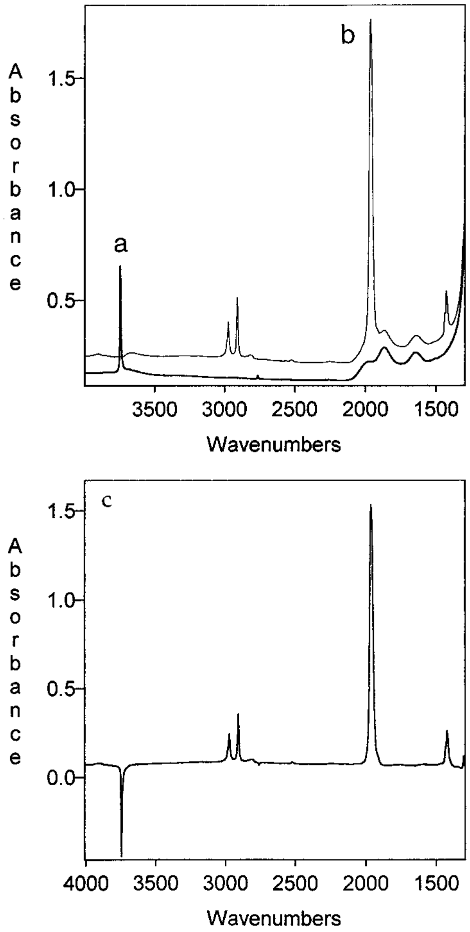

Figure 1. Transmission infrared spectra of (a) silica dehydroxylated at 500 °C, (b) after reaction with [$CH_3Rh(P(CH_3)_3)_2(CO)$], and (c) difference spectrum (b − a).

tated by the presence of multiple spectroscopic signatures. First, the frequency of the intense IR stretching mode of the CO ligand is highly sensitive to changes in the coordination environment and oxidation state of Rh.[20] The phosphine ligands provide information about the symmetry and mobility of chemisorbed species via ^{31}P solid-state NMR. In addition, ^{13}CO is readily incorporated for ^{13}C solid-state NMR studies of CO insertion reactions. In this paper, we present spectroscopic evidence that ligand exchange, oxidative addition, CO insertion, and reductive elimination are viable surface reaction pathways.

Results

Preparation and Characterization of *trans*-[≡SiORh-(P(CH$_3$)$_3$)$_2$(CO)]. The surface of partially dehydroxylated silica, pretreated at 500 °C, is terminated by non-hydrogen-bonded hydroxyl groups, represented as ≡SiOH, and siloxane bridges, ≡SiOSi≡.[21] When bright yellow *trans*-$CH_3Rh(P(CH_3)_3)_2(CO)$ is sublimed onto this surface at 50 °C, the silica acquires a deep orange color. The progress of the reaction was monitored by in situ IR spectroscopy of a self-supporting silica disk. After desorption at 80 °C of unreacted starting material, the transmission spectrum shows a loss of intensity for the free surface hydroxyl groups, ν(OH), at 3747 cm^{-1}, and the appearance of bands due to the ν(C−H) and δ(CH_3) vibrations of the $P(CH_3)_3$ ligands at 2975, 2910, and 1425 cm^{-1}, Figure 1. The most intense band in the spectrum, at 1968 cm^{-1}, is assigned to the ν(CO) mode. The surface species responsible for these new bands is strongly adsorbed and cannot be removed by prolonged dynamic vacuum, even at 100 °C. These observations are consistent with irreversible grafting of the molecular complex onto the silica surface by reaction with its hydroxyl groups, eq 1.

$$\equiv SiOH + CH_3Rh(P(CH_3)_3)_2(CO) \rightarrow \equiv SiORh(P(CH_3)_3)_2(CO) + CH_4 \quad (1)$$

1

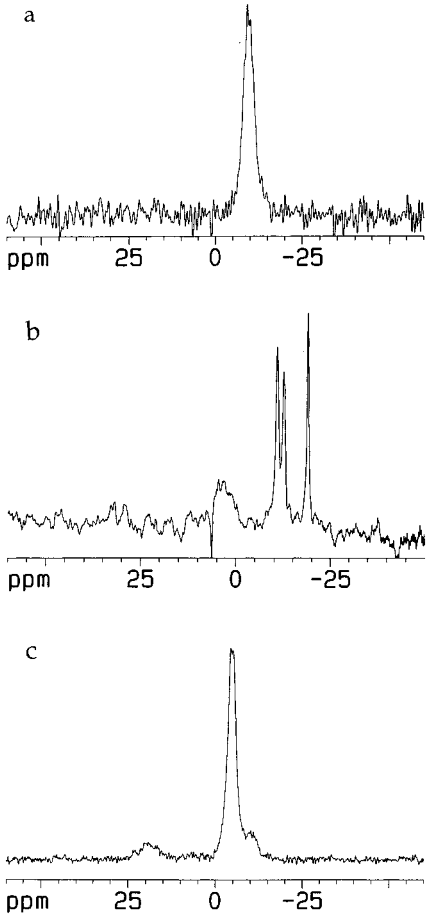

Figure 2. $^{31}P\{^1H\}$ MAS NMR spectra of [$\equiv SiORh(P(CH_3)_3)_2(CO)$] (spin rate 3.5 kHz) (a) in a vacuum, (b) in the presence of excess $P(CH_3)_3$, and (c) in the presence of 10 Torr of $HCl_{(g)}$.

Methane was observed in the gas phase and identified by its characteristic rovibrational spectrum.

The $^{31}P\{^1H\}$ MAS spectrum of **1** consists of a broad resonance at −10.1 ppm (fwhm 300 Hz) for which coupling to Rh is barely (but reproducibly) discernible, Figure 2a. MAS and CP/MAS spectra are identical, suggesting that there is a single Rh environment. The ^{13}C CP/MAS spectrum of **1** (enriched in ^{13}CO—see below) contains carbonyl and methyl resonances at 191.3 and 15.6 ppm, respectively, with no observable coupling, Figure 3a. The ^{13}C resonance for coordinated CO is strongly anisotropic, giving rise to intense spinning sidebands which render observation of the isotropic resonance difficult without ^{13}C enrichment.

Reaction with CO. Addition of excess ^{12}CO to **1** gave no spectral changes before or after evacuation. However, introduction of 10 Torr of ^{13}CO (containing 10% $^{13}C^{18}O$) led to the immediate disappearance of the strong ν(CO) band at 1968 cm^{-1} and the appearance of two new bands at 1920 and 1874 cm^{-1},

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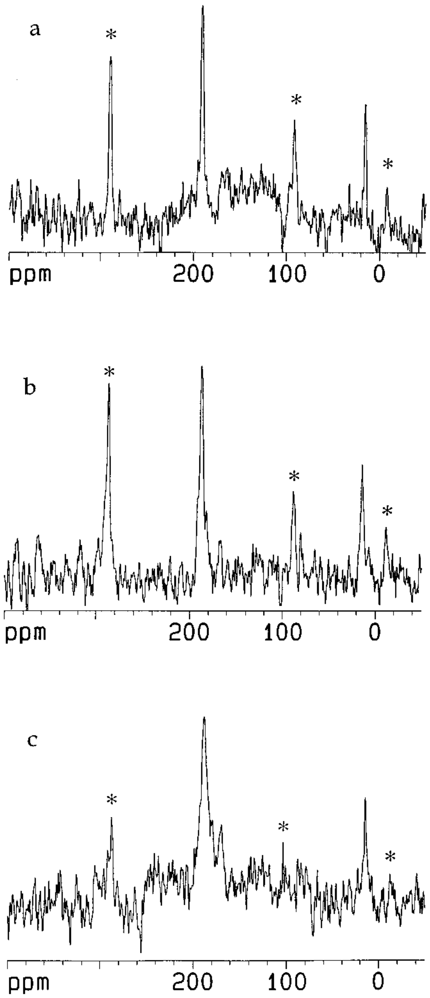

Figure 3. ^{13}C CP/MAS NMR spectra (spin rate 5 kHz) of (a) [$\equiv$SiORh(P(CH$_3$)$_3$)$_2$(^{13}CO)], **1**; (b) [$\equiv$SiORh(P(CH$_3$)$_3$)$_2$(^{13}CO)(CH$_3$)(I)], **8**; and (c) [$\equiv$SiORh(P(CH$_3$)$_3$)$_2$(^{13}CO)(^{13}COCH$_3$)(I)], **9**. Note: an asterisk indicates a spinning sideband.

Figure 4a. Addition of unlabeled CO restored the original spectrum. The reversible shift of the ν(CO) mode at 1968 to 1920/1874 cm^{-1} is consistent with facile exchange between coordinated ^{12}CO and ^{13}C^{16}O/^{13}C^{18}O from the gas phase, eq 2.

$$\equiv\text{SiORh(P(CH}_3)_3)_2(^{12}\text{CO}) + {}^{13}\text{CO} \rightleftharpoons \underset{\textbf{1-}^{\mathbf{13}}\textbf{CO}}{\equiv\text{SiORh(P(CH}_3)_3)_2(^{13}\text{CO})} + {}^{12}\text{CO} \quad (2)$$

The predicted isotope shifts for a diatomic ^{12}C^{16}O oscillator of frequency 1968 cm^{-1} are to 1923 (^{13}C^{16}O) and 1876 (^{13}C^{18}O) cm^{-1} (the latter accounts for the second, smaller carbonyl band in Figure 4a).

Reactions with Phosphines. Addition of excess P(CH(CH$_3$)$_2$)$_3$ to **1** followed by evacuation caused the position of the ν(CO) mode to shift from 1968 to 1948 cm^{-1} (Figure 5, parts a and b), consistent with the ligand replacement reaction shown in eq 3.

$$\underset{\mathbf{1}}{\equiv\text{SiORh(P(CH}_3)_3)_2\text{(CO)}} + 2\text{P(CH(CH}_3)_2)_3 \rightleftharpoons \underset{\mathbf{2}}{\equiv\text{SiORh(P(CH(CH}_3)_2)_3)_2\text{(CO)}} + 2\text{P(CH}_3)_3 \quad (3)$$

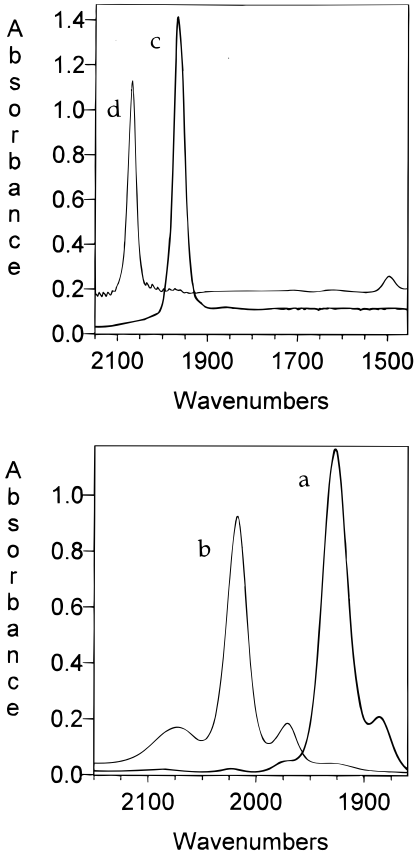

Figure 4. Transmission IR spectra of (a) [$\equiv$SiORh(P(CH$_3$)$_3$)$_2$(^{13}CO)], **1-^{13}CO**; (b) [$\equiv$SiORh(P(CH$_3$)$_3$)$_2$(^{13}CO)(H)(Cl)], **5-^{13}CO**; (c) [$\equiv$SiORh(P(CH$_3$)$_3$)$_2$(^{12}CO)], **1**; and (d) [$\equiv$SiORh(P(CH$_3$)$_3$)$_2$(CO)(D)(Cl)], **5-D**. The background spectrum of silica was removed by subtraction.

Bands characteristic of P(CH(CH$_3$)$_2$)$_3$ were also observed at 2965, 2933, 2910, and 2875 cm^{-1} (C$-$H stretching) and 1465, 1423, 1387, and 1370 cm^{-1} (C$-$H deformations).

The addition of excess P(CH$_3$)$_3$ to **2** was expected to regenerate **1**, accompanied by the reversion of the ν(CO) mode to its original position at 1968 cm^{-1}. Instead, after several cycles of P(CH$_3$)$_3$ addition followed by evacuation, a ν(CO) mode at 1958 cm^{-1} was obtained. This frequency is intermediate between those of **1** (1968 cm^{-1}) and **2** (1948 cm^{-1}), and is assigned to the mixed phosphine complex, [$\equiv$SiORh(P(CH$_3$)$_3$)(P(CH(CH$_3$)$_2$)$_3$)(CO)], **3**. In the C$-$H stretching and deformation regions, bands characteristic of both P(CH$_3$)$_3$ and P(CH(CH$_3$)$_2$)$_3$ were observed.

Interestingly, upon addition of P(CH$_3$)$_3$ to **2** and before evacuation, the ν(CO) band appears at even lower frequency, 1930 cm^{-1}, and is noticeably narrower. Soon after evacuation, the band at 1958 cm^{-1} reappears, Figure 5c; however, the complete conversion of the species responsible for the band at 1930 cm^{-1} to **3** requires prolonged evacuation (several hours at room temperature). The slowness of this reaction, unlike that of CO exchange, did not seem consistent with a simple substitution at Rh(I), and therefore prompted us to study the degenerate exchange reaction of **1** with P(CH$_3$)$_3$.

The addition of excess P(CH$_3$)$_3$ to **1** caused the color of the silica to change from orange to brilliant yellow. In addition to the broad ν(CO) band of **1** at 1968 cm^{-1}, a new ν(CO) mode appeared at 1934 cm^{-1}. The intensity of the original ν(CO) band at 1968 cm^{-1} depends on the amount of P(CH$_3$)$_3$ present; with a large excess of P(CH$_3$)$_3$, the original band disappears completely at the expense of the new, lower frequency band, Figure 5d. Upon evacuation, the yellow color fades, and the

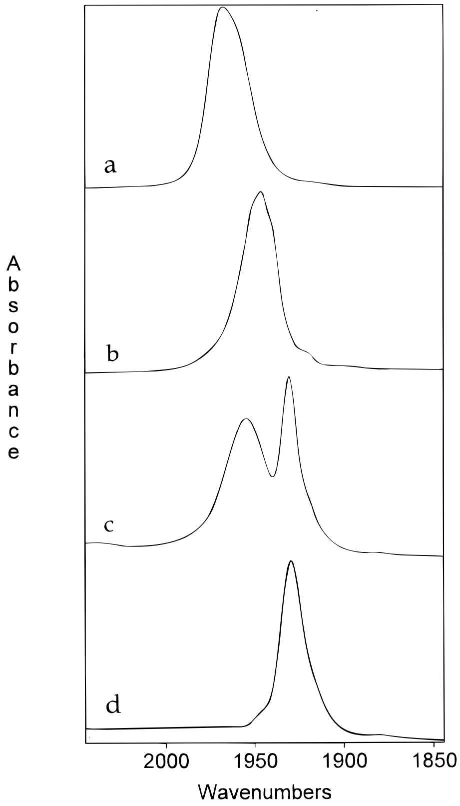

Figure 5. Transmission IR spectra in the ν(CO) region of (a) [$\equiv$SiORh(P(CH$_3$)$_3$)$_2$(CO)], **1**; (b) **1** treated with excess P(CH(CH$_3$)$_2$)$_3$ followed by evacuation; (c) sample from (b) treated with excess P(CH$_3$)$_3$ followed by evacuation; and (d) **1** treated with excess P(CH$_3$)$_3$.

band at 1934 cm^{-1} slowly disappears while the band at 1968 cm^{-1} simultaneously reappears. Upon prolonged evacuation (several hours at room temperature) the latter eventually becomes the only carbonyl band in the spectrum, although with slightly less than its original intensity. The ^{31}P{^{1}H} MAS spectrum recorded after **1** was treated with a very large excess of P(CH$_3$)$_3$, and before evacuation, contains three narrow resonances at -10.7, -12.5, and -18.8 ppm in an intensity ratio of 1:1:1, Figure 2b, in addition to free P(CH$_3$)$_3$ at -62.1 ppm.

The narrowing of IR and MAS NMR spectral lines in the presence of excess P(CH$_3$)$_3$, compared to the spectra of **1**, suggests that the surface rhodium complex has acquired significant mobility. In fact, the static ^{31}P{^{1}H} NMR spectrum recorded with excess P(CH$_3$)$_3$ is similar (only slightly broader) to the MAS spectrum, which is a result quite different from any of the grafted rhodium phosphine complexes we have examined thus far.[14,22] These observations suggest that P(CH$_3$)$_3$ disrupts the chemisorption of **1** to give a cationic rhodium(I) complex, **4**, which is associated with the silica surface by ion pairing. The formation of **4** may occur by initial coordination of the phosphine to **1**, followed by dissociation from the surface, eq 4.

$$\underset{\mathbf{1}}{\equiv\mathrm{SiORh(P(CH_3)_3)_2(CO)}} + \mathrm{P(CH_3)_3} \rightleftharpoons \{\equiv\mathrm{SiORh(P(CH_3)_3)_3(CO)}\} \rightleftharpoons \underset{\mathbf{4}}{\equiv\mathrm{SiO^-[Rh(P(CH_3)_3)_3(CO)]^+}} \quad (4)$$

We assign the doublet centered at -11.6 ppm to the mutually trans phosphine ligands of **4**, which are coupled to Rh with $J_{\mathrm{Rh-P}}$ = 145 Hz. The resonance at -18.8 ppm is assigned to the phosphine trans to CO, for which no coupling to Rh is detected.[23] No P$-$P coupling was observed.

To confirm the identity of **4**, it was prepared independently from a known cationic surface complex. Treatment of $\equiv$SiORh(P(CH$_3$)$_3$)$_3$) with H$_2$ in the presence of excess P(CH$_3$)$_3$ has been shown to give quantitatively the surface ion pair ($\equiv$SiO$^-$)[Rh(P(CH$_3$)$_3$)$_4$H$_2$]$^+$.[22] After evacuation of volatiles, this complex was treated with CO. The IR spectrum of the product was identical with that shown in Figure 5d.

Reaction with HCl and Cl$_2$. When excess anhydrous HCl$_{(g)}$ was added to **1**, the ν(CO) band at 1968 cm^{-1} disappeared completely, while a new band of slightly lower intensity appeared at 2066 cm^{-1}, Figure 4c. Upon evacuation, the ν(CO) band immediately returned to its original position at 1968 cm^{-1}. These spectroscopic changes are consistent with reversible oxidative addition of HCl, eq 5.

$$\underset{\mathbf{1}}{\equiv\mathrm{SiORh(P(CH_3)_3)_2(CO)}} + \mathrm{HCl} \rightleftharpoons \underset{\mathbf{5}}{\equiv\mathrm{SiORh(P(CH_3)_3)_2(CO)(H)(Cl)}} \quad (5)$$

We do not see a ν(Rh$-$H) vibration in the IR spectrum of **5**. Its ^{31}P{^{1}H} spectrum is a barely resolved doublet at -4.7 ppm ($J_{\mathrm{Rh-P}}$ = ca. 120 Hz), Figure 2c. There is no IR evidence for formation of a formyl complex, whose ν(CO) mode should appear below 1750 cm^{-1}.[24]

When DCl instead of HCl was added to **1**, the ν(CO) band at 2066 cm^{-1} appeared as expected, superimposed on the gas-phase rovibrational spectrum of DCl, as well as a weak band at 1496 cm^{-1}, Figure 4d. The latter is assigned to the ν(Rh$-$D) mode of $\equiv$SiORh(P(CH$_3$)$_3$)$_2$(CO)(D)(Cl), **5(D)**, and the band disappears upon evacuation. From a simple reduced mass calculation, we predict that the corresponding ν(Rh$-$H) mode of **5(H)** should appear at ca. 2100 cm^{-1}, and is therefore obscured by the intense ν(CO) band. To observe ν(Rh$-$H) directly, **1** was first exposed to ^{13}CO (containing 10% ^{13}C^{18}O), then to HCl (Figure 4, parts a and b). The ν(CO) modes of **5(^{13}CO)** and **5(^{13}C^{18}O)**, at 2018 and 1971 cm^{-1}, do not mask ν(Rh$-$H). The latter is seen clearly at 2072 cm^{-1}, close to its predicted position.

Addition of excess HCl to **2** caused only a slight decrease in ν(CO) at 1948 cm^{-1}, accompanied by the appearance of two weak new bands at 2058 and 2086 cm^{-1}, assigned to ν(CO) and ν(RhH), respectively.

When Cl$_{2(g)}$ was added to **1**, the ν(CO) band at 1968 cm^{-1} disappeared, to be replaced by a new and slightly less intense ν(CO) band at 2087 cm^{-1}. We infer that oxidative addition of Cl$_2$ occurred, eq 6.

$$\underset{\mathbf{1}}{\equiv\mathrm{SiORh(P(CH_3)_3)_2(CO)}} + \mathrm{Cl_2} \rightarrow \underset{\mathbf{6}}{\equiv\mathrm{SiORh(P(CH_3)_3)_2(CO)(Cl)_2}} \quad (6)$$

The reaction is not reversible, even after prolonged evacuation. No spectral changes were observed when **1** was exposed to 100 Torr of H$_2$ at room temperature.

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(23) In a molecular complex of similar symmetry, [CH$_3$Rh(P(CH$_3$)$_3$)$_3$], the trans phosphines resonate at -10.40 ppm ($J_{\mathrm{Rh-P}}$ = 151 Hz) and the cis phosphine at -15.74 Hz ($J_{\mathrm{Rh-P}}$ = 123 Hz). Price, R. T.; Andersen, R. A.; Muetterties, E. L. *J. Organomet. Chem.* **1989**, *376*, 407$-$417.

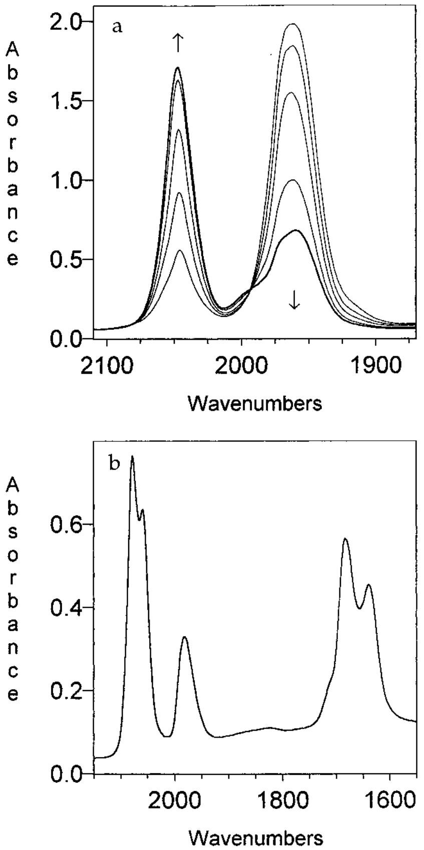

Figure 6. (a) Transmission IR spectra, recorded over a period of 3 h, of [$\equiv$SiORh(P(CH$_3$)$_3$)$_2$(CO)] treated with CH$_3$I and (b) the previous sample after addition of CO followed by evacuation.

Reactions with Organic Halides. The reaction of **1** with CCl$_3$Br results in an immediate shift of ν(CO) to 2085 cm^{-1}, assigned to [$\equiv$SiORh(P(CH$_3$)$_3$)$_2$(CO)(Br)(CCl$_3$)], **7**. This surface reaction is not reversible under dynamic vacuum.

In contrast, the addition of CH$_3$I to **1** causes a slow decrease in intensity at 1968 cm^{-1} and the simultaneous appearance of a new band at 2048 cm^{-1}, Figure 6a. The new band is assigned to the ν(CO) mode of the oxidative addition product [$\equiv$SiORh(P(CH$_3$)$_3$)$_2$(CO)(CH$_3$)(I)], **8**, eq 7.

$$\underset{\mathbf{1}}{\equiv\text{SiORh(P(CH}_3)_3)_2\text{(CO)}} + \text{CH}_3\text{I} \rightarrow \underset{\mathbf{8}}{\equiv\text{SiORh(P(CH}_3)_3)_2\text{(CO)(CH}_3\text{)(I)}} \quad (7)$$

Time-resolved IR spectroscopy revealed an isosbestic point at 1993 cm^{-1}, Figure 6a. The ^{31}P spectrum of **8** consists of a single resonance at -9.5 ppm, indicating that the phosphine ligands remain mutually trans. The ^{13}C spectrum of **1(^{13}CO)** after reaction with CH$_3$I consists of two resonances at 187.4 and 14.2 ppm, Figure 3b, assigned to *C*O and P(*C*H$_3$)$_3$ signals, respectively. The surface species **8** is stable under dynamic vacuum at room temperature, but undergoes reductive elimination to regenerate **1** (with reappearance of the band at 1968 cm^{-1}) upon heating in a vacuum at 60 °C.

Although **8** does not undergo spontaneous CO insertion/methyl migration, it was possible to induce the reaction by addition of excess phosphine or CO. Thus, when excess P(CH$_3$)$_3$ was added at room temperature to **8**, the ν(CO) band at 2048 cm^{-1} immediately disappeared and new bands appeared at 1674 and 1653 cm^{-1}. These frequencies are characteristic of the ν(CO) modes of acylrhodium(III) complexes, which may be formed by CO insertion as shown in eq 8.

$$\underset{\mathbf{8}}{\equiv\text{SiORh(P(CH}_3)_3)_2\text{(CO)(CH}_3\text{)(I)}} + \text{P(CH}_3)_3 \rightleftharpoons \underset{\mathbf{9}}{\equiv\text{SiORh(P(CH}_3)_3)_3\text{(COCH}_3\text{)(I)}} \quad (8)$$

The observation of two ν(CO) bands for **9** implies the presence of two geometric or rotational isomers.[25]

On a slower time scale (several hours) in the presence of P(CH$_3$)$_3$, the spectrum of **9** evolved such that a new band appeared at 1935 cm^{-1}, which we have assigned to **4** (see above). Thus it appears that the presence of P(CH$_3$)$_3$ eventually facilitates reductive elimination of CH$_3$I, eqs 8 and 9.

$$\underset{\mathbf{9}}{\equiv\text{SiORh(P(CH}_3)_3)_2\text{(COCH}_3\text{)(I)}} + \text{P(CH}_3)_3 \rightarrow \underset{\mathbf{4}}{\equiv\text{SiO}^-[\text{Rh(P(CH}_3)_3)_3\text{(CO)]}^+} + \text{CH}_3\text{I} \quad (9)$$

CO insertion was also induced by the reaction of **8** with CO. The IR spectrum, Figure 6b, shows two acyl ν(CO) bands at 1682 and 1640 cm^{-1}, and two new terminal carbonyl ν(CO) bands at 2077 and 2059 cm^{-1}, assigned to isomers of the acylcarbonylrhodium(III) complex **10**, eq 10.

$$\underset{\mathbf{8}}{\equiv\text{SiORh(P(CH}_3)_3)_2\text{(CO)(CH}_3\text{)(I)}} + \text{CO} \rightarrow \underset{\mathbf{10}}{\equiv\text{SiORh(P(CH}_3)_3)_2\text{(CO)(COCH}_3\text{)(I)}} \quad (10)$$

We verified independently the attribution of the surface acyl bands to **10** via the oxidative addition of CH$_3$C(O)Cl to **1**. As expected, the ν(CO) band of **1** at 1968 cm^{-1} disappeared and new bands appeared at 2078, 2068 (sh), 1675, and 1653 cm^{-1}. The ^{31}P{^{1}H} MAS spectrum of **10** contains a resonance at -24.1 ppm, assigned to mutually trans phosphine ligands. In comparison, we previously reported a chemical shift of -24.3 for the trans phosphine ligands of ($\equiv$SiO)$_2$Rh(P(CH$_3$)$_3$)$_3$(CH$_2$-CH=CH$_2$).[14] The ^{13}C CP/MAS spectrum of **10(^{13}CO)** (prepared by oxidative addition of CH$_3$I to **1(^{13}CO)** followed by addition of ^{13}CO) has two carbonyl resonances at 187.8 (*C*O) and 169.2 ppm (*C*OCH$_3$), as well as a resonance at 14.1 (P(*C*H$_3$)$_3$) ppm, Figure 3c.

Upon evacuation of the reactor containing **10**, a new band appeared in the IR spectrum at 1961 cm^{-1}, Figure 6b. This frequency corresponds to the ν(CO) mode assigned to **1** (see above), formed by reductive elimination of acetyl iodide from **10**, eq 11.

$$\underset{\mathbf{10}}{\equiv\text{SiORh(P(CH}_3)_3)_2\text{(CO)(COCH}_3\text{)(I)}} \rightarrow \underset{\mathbf{1}}{\equiv\text{SiORh(P(CH}_3)_3)_2\text{(CO)}} + \text{CH}_3\text{C(O)I} \quad (11)$$

When allyl chloride was added to **1**, the immediate disappearance of ν(CO) at 1966 cm^{-1} was observed. A new band appeared at 2047 cm^{-1}, assigned to the oxidative addition product [$\equiv$SiORh(P(CH$_3$)$_3$)$_2$(CO)(CH$_2$CH=CH$_2$)(Cl)], **11**. In contrast to the behavior of **8**, the allylrhodium(III) complex **11** is not stable. The band at 2047 cm^{-1} was observed to first

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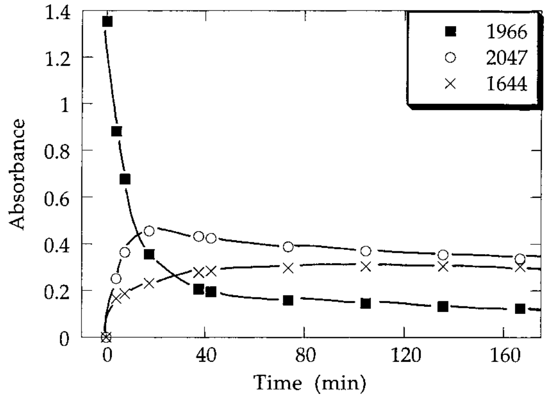

Figure 7. Time-resolved evolution of IR bands in the ν(CO) region following addition of allyl chloride to $\equiv$SiORh($P(CH_3)_3)_2$(CO).

increase then decrease in intensity, Figure 7. At the same time, a new band grew in at 1644 cm^{-1}, assigned to [$\equiv$SiORh($P(CH_3)_3)_2$($COCH_2CH{=}CH_2$)(Cl)], **12**.[26]

Surface reactions are depicted in Scheme 1 and spectral characteristics of surface species are summarized in Table 1.

Discussion

Formation of a Well-Defined Grafted Complex. The ν(CO) frequency of the silica-supported organometallic fragment **1**, at 1968 cm^{-1}, is similar to that of a molecular analogue, *trans*-ClRh($P(CH_3)_3)_2$(CO), at 1960 cm^{-1}.[27] In contrast, the ν(CO) mode of the starting material $CH_3Rh(P(CH_3)_3)_2(CO)$ occurs at 1948 cm^{-1},[27] so that the absence of a band at this frequency in the spectrum of the modified silica, as well as the appearance of methane in the gas phase, is evidence for chemisorption rather than physisorption of **1** on silica. The ^{31}P and ^{13}C chemical shifts of **1** also closely resemble those of *trans*-[ClRh($P(CH_3)_3)_2$(CO)],[27] Table 1.

The irreversible gas−solid reaction of [$CH_3Rh(P(CH_3)_3)_2$(CO)] with the surface hydroxyl groups of silica is reminiscent of the formation of oxide-supported bis(allyl)rhodium(III) by the reaction of [Rh(η^3-$C_3H_5)_3$] with the oxide, in a reaction that liberates propene, eq 12.[28−30]

$$2(\equiv\mathrm{SiOH}) + \mathrm{Rh}(\eta^3\text{-}\mathrm{C_3H_5})_3 \rightarrow \equiv\mathrm{SiO}(\equiv\mathrm{SiOH})\mathrm{Rh}(\eta^3\text{-}\mathrm{C_3H_5})_2 + \mathrm{C_3H_6} \quad (12)$$

The reaction of [$\equiv$SiO($\equiv$SiOH)Rh(η^3-$C_3H_5)_2$] with $P(CH_3)_3$ was reported to yield the tris(phosphine) complex [$\equiv$SiORh($P(CH_3)_3)_3$] as the major product.[14] The reaction of the latter surface organometallic fragment with CO yields **1** by substitution of a phosphine ligand, eq 13.[31]

$$\equiv\mathrm{SiORh(P(CH_3)_3)_3} + \mathrm{CO} \rightarrow \underset{\mathbf{1}}{\equiv\mathrm{SiORh(P(CH_3)_3)_2(CO)}} + \mathrm{P(CH_3)_3} \quad (13)$$

The IR and ^{31}P NMR characteristics of **1** formed by this route are identical with those of **1** prepared directly by grafting [$CH_3Rh(PMe_3)_2$(CO)] on to silica, as in eq 1.

Ligand Substitutions. A rapid exchange of carbonyl ligands has been reported in the reaction of [ClRh($P(CH_3)_3)_2$(CO)] with ^{13}CO.[19] Therefore it is not surprising that a similar facile reaction was found for the surface species **1**. The five-coordinate intermediate of an S_N2 mechanism at a 16-electron metal center should be readily accessible on the silica surface, as [$\equiv$SiORh($P(CH_3)_3)_2$(^{12}CO)(^{13}CO)].[32]

The more basic triisopropylphosphine ligand is a stronger σ-donor than $P(CH_3)_3$, and this property is expected to result in greater back-donation of π-electron density from Rh to CO. The frequency shift of ν(CO) from 1968 to 1948 cm^{-1} upon exchange of the phosphine ligands of **1** is consistent with this effect. In analogous molecular complexes, the difference in ν(CO) frequencies between [ClRh($P(CH_3)_3)_2$(CO)] and [ClRh($P(CH(CH_3)_2)_3)_2$(CO)] is similar, from 1960 to 1946 cm^{-1}.[33]

Cation−Neutral Interconversion. We did not expect to observe a reaction between **1** and $P(CH_3)_3$, since the exchange reaction is degenerate and the five-coordinate intermediate should lose phosphine readily. The IR and NMR spectra of the surface species are consistent with the cation **4** but not with ($\equiv$SiO$^-$)[Rh($P(CH_3)_3)_4$]$^+$.[34] Also, the reversibility of the reaction by prolonged evacuation is not consistent with loss of the CO ligand. The formation of **4** is not unprecedented in the molecular chemistry of Rh. Interconversion between neutral and cationic forms of four-coordinate rhodium complexes was reported for [ClRh($P(CH_3)_3)_3$] and Cl$^-$[Rh($P(CH_3)_3)_4$]$^+$ by addition and removal of excess $P(CH_3)_3$.[35] The ability of the silica surface to act as a counteranion to a cationic rhodium complex has also been demonstrated.[22] Despite its positive charge, **4** has a lower ν(CO) frequency than **1** because of the coordination of CO trans to phosphine, which is a stronger σ-donor than the "siloxo" ligand derived from the silica surface. Finally, the independent preparation of **4** from another surface cationic complex is consistent with the reductive elimination shown in eq 14.

$$(\equiv\mathrm{SiO^-})[\mathrm{Rh(P(CH_3)_3)_4(H)_2}]^+ + \mathrm{CO} \rightarrow \underset{\mathbf{4}}{(\equiv\mathrm{SiO^-})[\mathrm{Rh(P(CH_3)_3)_3(CO)}]^+} + \mathrm{H_2} + \mathrm{P(CH_3)_3} \quad (14)$$

In molecular chemistry, [Rh($P(CH_3)_3)_3$(CO)]$^+$ has not yet been isolated. The reaction of [ClRh($P(CH_3)_3)_2$(CO)] with excess $P(CH_3)_3$ was reported to give an unstable material that decomposed readily.[36] However, cationic carbonyl complexes of Rh(I) are known with other phosphine ligands, for example, [Rh($P(C_6H_5)_3)_3$(CO)]$^+$ and [Rh($P(C_6H_5)_2(CH_3))_3$(CO)]$^+$.[37]

Oxidative Addition. Oxidative addition to **1** of various substrates results in a shift of ν(CO) by ca. 100 cm^{-1} to higher frequency, corresponding to a large decrease in back-bonding from Rh to CO in the Rh(III) surface complexes. In addition,

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(26) Note that both acyl ν(CO) and allylic ν(C=C) vibrations are expected in this region. The observed increase in intensity may be due to either or, more likely, both.

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Scheme 1

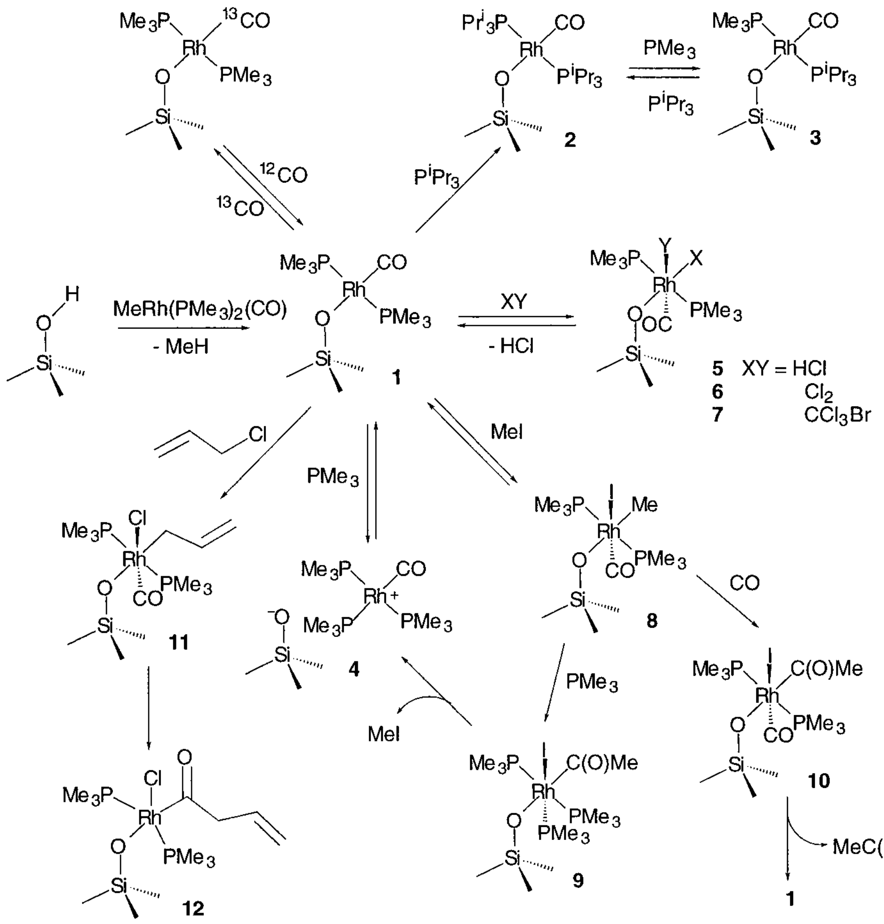

Table 1. IR and NMR Spectral Characteristics of Surface Species

surface complexes[a]	ν(CO)[b], cm^{-1}	^{31}P δ/ppm	^{13}C δ/ppm
$\equiv$SiORh(P)$_2$(CO), **1**	1968 (1920)	−10.1	191.3, 15.6
$\equiv$SiORh(P′)$_2$(CO), **2**	1948		
$\equiv$SiORh(P)(P′)(CO), **3**	1958		
$\equiv$SiO$^-$[Rh(P)$_3$(CO)]$^+$, **4**	1934		
$\equiv$SiORh(P)$_2$(CO)(H)(Cl), **5**	2066 (2018)	−4.7	
$\equiv$SiORh(P′)$_2$(CO)(H)(Cl)	2058		
$\equiv$SiORh(P)$_2$(CO)(Cl)$_2$, **6**	2087		
$\equiv$SiORh(P)$_2$(CO)(Br)(CCl$_3$), **7**	2085		
$\equiv$SiORh(P)$_2$(CO)(CH$_3$)(I), **8**	2048	−9.5	187.4, 14.2
$\equiv$SiORh(P)$_3$(COCH$_3$)(I), **9**	1674, 1653		
$\equiv$SiORh(P)$_2$(CO)(COCH$_3$)(I), **10**	2077, 2059, 1682, 1640	−24.1	187.8, 169.2, 14.1
$\equiv$SiORh(P)$_2$(CO)(CH$_2$CH=CH$_2$)(Cl), **11**	2047		
$\equiv$SiORh(P)$_2$(COCH$_2$CH=CH$_2$)(Cl), **12**	1644		

[a] P is P(CH$_3$)$_3$ and P′ is P(CH(CH$_3$)$_2$)$_3$. [b] Frequencies in parentheses are for ^{13}CO-substituted species.

the ^{31}P chemical shift moves downfield. These behaviors have been observed in molecular chemistry. For example, the reversible oxidative addition of HCl$_{(g)}$ to [ClRh(P(CH$_3$)$_3$)$_2$(CO)] gives [Rh(P(CH$_3$)$_3$)$_2$(CO)(H)(Cl)$_2$], with δ −3.34 ppm (d, $^1J_{\mathrm{Rh-P}}$ = 81.1 Hz).[27] The ν(CO) frequency of a similar complex, [Rh(P(CH$_2$CH$_3$)$_3$)$_2$(CO)(H)(Cl)$_2$], was reported at 2050 cm^{-1}.[38] Formation of [$\equiv$SiORh(P(CH(CH$_3$)$_2$)$_3$)$_2$(CO)(H)(Cl)] is apparently less favorable than in the case of the P(CH$_3$)$_3$ analogue, perhaps due to the combined steric bulk of the P(CH(CH$_3$)$_2$)$_3$ and siloxo ligands. The molecular analogue [Rh(P(CH(CH$_3$)$_2$)$_3$)$_2$(CO)(H)(Cl)$_2$], although not isolated, was reported to have ν(CO) and ν(RhH) modes at 2037 and 2119 cm^{-1}, respectively,[38] compared to 2058 and 2086 cm^{-1} for the corresponding surface species.

There are two possible geometric isomers of the Rh(III) surface complex **5**. From NMR, we know that the phosphine ligands remain mutually trans, and we assume that the H and Cl ligands after oxidation addition are oriented cis to each other. The hydride ligand may then be either cis or trans to CO. For the molecular analogue [Rh(P(CH$_3$)$_3$)$_2$(CO)(H)(Cl)$_2$], formed by oxidative addition of HCl to [Rh(P(CH$_3$)$_3$)$_2$(CO)(Cl)], only one isomer was observed, in which the hydride is exclusively cis to CO.[27] We suggest that the analogous geometric isomer is formed on the silica surface, and we have no spectral evidence for the existence of more than one isomer on the silica surface,

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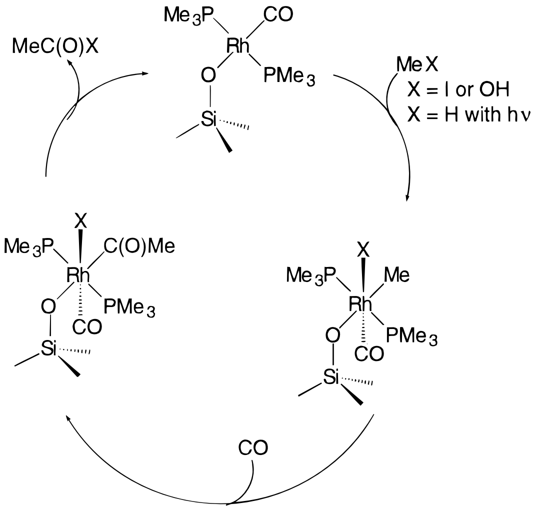
Scheme 2



although the IR and ^{31}P NMR line widths of our chemisorbed complexes are sufficiently broad that it is difficult to exclude the presence of a second isomer. Complex **5** showed no reactivity toward simple olefins at room temperature.

Unlike the reaction of **1** with HCl, the oxidative addition of Cl_2 is irreversible. The product **6** is analogous to the molecular complex $[Rh(P(CH_3)_3)_2(CO)(Cl)_3]$, with ν(CO) at 2055 cm^{-1}, which also does not eliminate Cl_2 spontaneously.[38] A similar irreversible reaction was observed with CCl_3Br, which also has precedent in the formation of the molecular complex $[ClRh(P(CH_3)_3)_2(CO)(Br)(CCl_3)]$, with ν(CO) at 2084 cm^{-1}.[39] The product **6** also showed no reactivity toward olefins at room temperature.

Formation of Acyl Complexes. The observation of an isosbestic point in the reaction of CH_3I with **1** is evidence for a simple oxidative addition with no intermediates. Subsequent CO insertion is not spontaneous, but induced by excess CO or $P(CH_3)_3$ to give two acyl isomers. Migratory insertion of CO into the Rh−CH_3 bond was calculated to be the rate-limiting step in a study of methane carbonylation by $Rh(PH_3)_2Cl$.[40] A molecular analogue, $[RhCl_2(COCH_3)(CO)(P(CH_3)_2Ph)_2]$, is also reported to have two IR bands in the acyl region at 1680 and 1652 cm^{-1}.[41] In principle, a heterogeneous process for catalytic carbonylation of methyl iodide, methanol, or even photocatalytic carbonylation of methane[10,17] could be based on reactions 9 and 12−13, as shown in Scheme 2.

In contrast to the chemistry of CH_3I, the biphasic kinetic behavior observed in the reaction of **1** with allyl chloride, interpreted as oxidative addition followed by spontaneous CO insertion, reflects the tendency of alkyl migration in transition metal carbonyl complexes to become more favorable as the length of the alkyl chain increases.[24,42] The ability of silica-supported allylrhodium complexes to undergo spontaneous CO insertion has been reported.[8]

Conclusion

A silica-supported Rh(I) complex has been shown to undergo ligand substitution, reversible interconversion of neutral and cationic forms, oxidative addition, CO insertion, and reductive elimination. The crucial requirement for these studies is a structurally well-defined surface complex as reactant. We fulfilled this requirement by using a molecular precursor whose structure remains intact after grafting onto the silica surface. Although we cannot obtain direct structural evidence for surface species, reactions can be identified on the silica surface by using complementary spectroscopic techniques and comparisons to molecular chemistry. In this work, the electronic properties of the silica "ligand" are similar to those of chloride in molecular chemistry, although the two differ greatly in steric requirements. Most of the surface transformations are strictly analogous to well-known reactions in molecular chemistry, but the surface complex **1** is unique in being able to convert between stable chemisorbed neutral and ionic forms. The latter is retained on the surface by electrostatic attraction, yet is significantly mobile.

Experimental Section

The starting material $[CH_3Rh(P(CH_3)_3)_2(CO)]$ was prepared according to a slightly modified version of the published procedure.[27] After reaction of $[ClRh(P(CH_3)_3)_2(CO)]$ with $(CH_3)_2Mg$ in THF at −78 °C under an inert atmosphere of N_2, the solution was filtered, pentane was added, and the solution was filtered again. The pentane was evaporated and the product sublimed at 80 °C (10^{-4} Torr). ^{13}CO (99% ^{13}C, 10% ^{18}O) and DCl (98% D) were obtained from Cambridge Isotopes. CO (Air Products, 99%) and anhydrous HCl (Matheson, 99%) were used as received. All other reagents were purchased from Aldrich. Each was transferred into an evacuated glass bulb equipped with a grease-free high-vacuum Teflon stopcock. All reactions were performed in the absence of solvents or inert atmospheres, using vapor phase transfers of gases and volatile liquid reagents via a high vacuum manifold.

The silica used in all experiments was Degussa Aerosil-200, a pyrogenic silica with a specific surface area of 200 m^2/g. For infrared experiments, ca. 25 mg of silica was pressed at 125 kg/cm^2 into a 16 mm self-supporting disk, which was mounted in an in-situ infrared cell. The silica disk was calcined in 200 Torr of O_2 at 500 °C for 2 h to remove adsorbed hydrocarbon impurities, then evacuated at 500 °C and 10^{-4} Torr for at least 2 h in order to effect a partial dehydroxylation of the surface. The rhodium complex was sublimed at 50 °C in vacuo from a breakseal onto the silica disk, and the unreacted portion was desorbed at 80 °C to a liquid N_2 trap. For NMR experiments, ca. 100 mg of silica was compacted at 125 kg/cm^2 then ground in a mortar. The silica was calcined and dehydroxylated in a Schlenk-tube reactor equipped with a high-vacuum ground-glass stopcock and a 5 mm Pyrex NMR tube welded perpendicular to the Schlenk tube. After each reaction, ca. 20 mg of silica was transferred in vacuo into the NMR tube, which was then sealed off at 28 mm lengths. The sealed NMR samples were placed in long (30 mm) zirconia rotors which fit into a special probe assembly.

Infrared spectra were recorded on a Mattson Research Series FT-IR spectrometer, which was continually purged with CO_2-free dry air. Typical spectral parameters are 32 scans at 2 cm^{-1} resolution, using a DTGS detector. Solid-state NMR spectra were recorded on a Bruker ASX-200. ^{13}C (frequency 50.32 MHz) CP/MAS (cross-polarization/magic-angle spinning) NMR spectra were collected using a 4.0 μs pulse followed by a proton 90° pulse of approximately 3.9 μs. Spinning sidebands were identified by varying the spin rate between 2500 and 5000 Hz. ^{31}P (frequency 81.0 MHz) MAS spectra were recorded with high-power proton decoupling and a 4 μs 90° pulse. ^{31}P CP/MAS spectra were recorded with a proton 90° pulse of 4.4 μs and a contact time of 2 ms. Static spectra were recorded with a 4 s delay and a 90° proton pulse of 4.7 μs.

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