# Hydroformylation of 1-Octene under Atmospheric Pressure Catalyzed by Rhodium Carbonyl Thiolate Complexes Tethered to Silica

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The silica-tethered rhodium thiolate complex catalysts Rh−S/$SiO_2$ and Rh−S−P/$SiO_2$ were prepared by the condensation of $SiO_2$ with $Rh_2[\mu\text{-}S(CH_2)_3Si(OCH_3)_3]_2(CO)_4$ (Rh−S) or $Rh_2[\mu\text{-}S(CH_2)_3Si(OCH_3)_3]_2[Ph_2P(CH_2)_3Si(OC_2H_5)_3]_2(CO)_2$ (Rh−S−P). These tethered complex catalysts exhibit high activity for the hydroformylation of 1-octene in the presence of phosphine donor ligands under the mild conditions of 60 °C and 1 atm. IR (DRIFT) spectral studies of the catalysts used indicate that tethered monorhodium dicarbonyl thiolate complexes of the type $Rh(SR)(CO)_2(PR'_3)$ are the predominant species on the surface for the catalysts that have the highest hydroformylation activity. The catalysts are easily separated from the reaction mixtures, and the Rh−S/$SiO_2$ catalyst maintains its activity through at least three cycles over a total period of 69 h, during which time there are 1273 (mol of aldehyde/mol of Rh) turnovers. Effects of the phosphine ligand and $PR'_3$/Rh mole ratio on the hydroformylation rate, conversion, and chemo- and regioselectivity for aldehyde products were also investigated.

## Introduction

Hydroformylation of olefins is an important and well-known process for the production of aldehydes and alcohols.[1] Much effort has been focused on the use of rhodium complexes as catalysts, because they often exhibit high activity as compared to other transition-metal catalysts.[2−7] Although homogeneous rhodium catalysts, in many cases, are more active and selective in the hydroformylation of olefins than are heterogeneous ones, an important technical problem is the separation and recovery of the soluble catalysts. Especially in the case of rhodium-complex-catalyzed hydroformylations of higher olefins, the separation of the catalyst from the high-boiling aldehydes requires vigorous distillation conditions which result in the degradation of the catalyst with concomitant loss of rhodium. One approach to solving this problem is to anchor the homogeneous complex catalyst on an insoluble support.

It is well-known that the rhodium thiolate complexes $[Rh(\mu\text{-}SR)(L)(L')]_2$ (L, L′ = COD or L = CO, L′ = $PR_3$; COD = cyclooctadiene) are active catalyst precursors for the hydroformylation of alkenes under conditions of low pressure and temperature (5 bar, 80 °C).[8−12] However, only two reports dealing with the application of immobilized rhodium thiolate complex catalysts in hydroformylation have appeared so far. Blum et al.[13] reported that a silica-bound rhodium complex with one bridging thiolate and one bridging chloro ligand ($Rh_2(CO)_2(PBu^t_3)_2(\mu\text{-}Cl)(\mu\text{-}SR)$, R = $CH_2CH_2CH_2Si(OC_2H_5)_3$) is active for the hydroformylation of cyclohexene under 80 atm of CO/$H_2$ and 120 °C. Also, the immobilized rhodium thiolate catalyst prepared from phosphinated cross-linked polystyrene and $Rh_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_4$ was used to catalyze the hydroformylation (80 °C, 5 bar) of olefins.[8b] In the present paper, we report that silica-tethered rhodium carbonyl thiolate complex catalysts prepared by the condensation of silica with $Rh_2[\mu\text{-}S(CH_2)_3Si(OCH_3)_3]_2(CO)_4$ or $Rh_2[\mu\text{-}S(CH_2)_3Si(OCH_3)_3]_2[Ph_2P(CH_2)_3Si(OC_2H_5)_3]_2(CO)_2$ efficiently catalyze the

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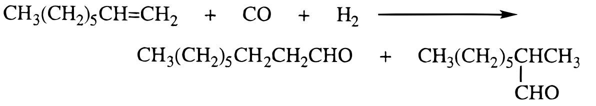
hydroformylation (eq 1) of 1-octene in the presence of a



$$CH_3(CH_2)_5CH{=}CH_2 + CO + H_2 \longrightarrow CH_3(CH_2)_5CH_2CH_2CHO + CH_3(CH_2)_5\underset{\underset{CHO}{|}}{C}HCH_3$$

(1)

phosphine or phosphite ligand under the mild conditions of 60 °C and 1 atm total pressure of $H_2$ and CO. To our knowledge, these are the first examples of immobilized rhodium complex catalysts that exhibit high activities for the hydroformylation of olefins under atmospheric pressure.

## Experimental Section

All syntheses of rhodium complex catalysts were performed using standard Schlenk techniques under an argon atmosphere. $Rh_2Cl_2(CO)_4$ was purchased from Strem. Silica gel 100 (BET surface area, 400 $m^2/g$) and (3-mercaptopropyl)trimethoxysilane were obtained from Fluka. $Ph_2P(CH_2)_3Si(OC_2H_5)_3$ was prepared according to the literature method.[14] Solvents were dried by refluxing over $CaH_2$ under nitrogen prior to use. All other reagents were commercial samples and were used as purchased.

FTIR and DRIFT spectra were recorded on a Nicolet 560 spectrophotometer equipped with a TGS detector in the main compartment and an MCT detector in the auxiliary experiment module (AEM). The AEM housed a Harrick diffuse-reflectance accessory. The solution IR spectra were measured in the main compartment using a solution cell with NaCl salt plates. The DRIFT spectra were recorded on samples in the Harrick microsampling cup. A Varian 3400 GC interfaced to a Finnigan TSG 700 high-resolution magnetic sector mass spectrometer with electron ionization (70 eV) was used for all GC-MS measurements. Gas chromatographic analyses were performed with a HP-6890 GC using a 32 m HP-1 capillary column with an FID detector.

The rhodium contents of the silica-tethered catalysts were determined by atomic emission spectroscopy. Each sample was prepared for analysis by first treating the catalyst (50 mg) with 5 mL of aqua regia at 90 °C for 5−10 min; then 5 mL of aqueous HF (5%) was added to the mixture, which was heated at 90 °C for 5−10 min. The resulting solution was diluted with water to 25 mL.

**Preparation of [$Rh_2(\mu\text{-}S(CH_2)_3Si(OCH_3)_3)_2(CO)_4$] (Rh−S).** $Rh_2[\mu\text{-}S(CH_2)_3Si(OCH_3)_3]_2(CO)_4$ was prepared by a procedure similar to that used for the preparation of other rhodium alkane- or arenethiolato carbonyl complexes $Rh_2(\mu\text{-}SR)_2(CO)_4$.[15] To a stirred suspension of sodium hydride (11 mg (60 wt %), 0.27 mmol) in THF (30 mL) cooled by an ice bath was added dropwise (3-mercaptopropyl)trimethoxysilane (47 $\mu$L, 0.26 mmol). After the mixture was stirred for 20 min, a solution of $Rh_2Cl_2(CO)_4$ (50 mg, 0.13 mmol) in THF (10 mL) was added dropwise, and this mixture was stirred at room temperature for 30 min. The mixture was evaporated and chromatographed on silica gel. Elution with ether/hexanes (1/1) gave the yellow-brown Rh−S complex. IR ($\nu$(CO) in toluene): 2074 (m), 2056 (s), 2004 (s) $cm^{-1}$. $^1H$ NMR (in $CDCl_3$): $\delta$ 3.57 (s, 18H, $OCH_3$), 3.11 (t, 4H, $SCH_2$), 1.91 (m, 4H, $CH_2CH_2CH_2$), 0.82 (m, 4H, $CH_2Si$). Anal. Calcd for $C_{16}H_{30}O_{10}S_2Rh_2$: C, 27.12; H, 4.27. Found: C, 27.48; H, 4.82.

**Preparation of *cis*-$Rh_2[\mu\text{-}S(CH_2)_3Si(OCH_3)_3]_2[Ph_2P(CH_2)_3Si(OC_2H_5)_3]_2(CO)_2$ (Rh−S−P).** A solution of Rh−S (0.10 g, 0.14 mmol) and $Ph_2P(CH_2)_3Si(OC_2H_5)_3$ (0.11 g, 0.28 mmol) in 10 mL of toluene was stirred at room temperature for 2 h. After the solvent was evaporated under vacuum, the oily residue was washed with pentane (2 mL) and dried under vacuum at room temperature to give the oily red complex Rh−S−P. Anal. Calcd for $C_{56}H_{92}O_{14}P_2S_2Si_4Rh_2$: C, 46.37; H, 6.59. Found: C, 46.92; H, 6.47. IR ($\nu$(CO) in toluene): 1970 (s), 1956 (s) $cm^{-1}$. $^{31}P\ \{^1H\}$ NMR (in $CDCl_3$, 200 MHz): $\delta$ 21.92 (d, $J_{Rh-P}$ = 122 Hz). The $J_{Rh-P}$ value is about the same as that ($J_{Rh-P}$ = 121 Hz) of the rhodium phosphine complex $RhCl(CO)(Ph_2PCH_3)_2$, which was prepared according to a literature procedure.[16]

**Preparation of the Tethered Catalyst Rh−S/$SiO_2$.** The rhodium thiolate complex Rh−S (46 mg, 0.065 mmol) was refluxed with $SiO_2$ (0.8 g), which had been dried under vacuum at 100 °C for 2 h, in 15 mL of toluene for 4 h. After filtration, the solid was washed with toluene (4 × 10 mL) and then dried under vacuum at room temperature. The resulting silica-tethered rhodium carbonyl thiolate complex catalyst Rh−S/$SiO_2$ (Rh content 1.50 wt %) gave an IR spectrum (DRIFTS) with $\nu$(CO) bands at 2081 (m), 2064 (s), and 2020 (s) $cm^{-1}$, which are very similar in position and relative intensity to those (2074 (m), 2056 (s), and 2004 (s) $cm^{-1}$ in toluene) of the free $Rh_2[\mu\text{-}S(CH_2)_3Si(OCH_3)_3]_2(CO)_4$ complex.

**Preparation of the Tethered Catalyst Rh−S−P/$SiO_2$.** Rh−S−P/$SiO_2$ was prepared in the same way as that used for the preparation of Rh−S/$SiO_2$ but using Rh−S−P instead of Rh−S. The rhodium content of the catalyst was 2.45 wt %. The IR spectrum (DRIFTS) of Rh−S−P/$SiO_2$ exhibits one $\nu$(CO) band at 1978 $cm^{-1}$, which is quite different from that (1970 (s), 1956 (s) $cm^{-1}$ in toluene) for the precursor *cis*-$Rh_2[\mu\text{-}S(CH_2)_3Si(OCH_3)_3]_2[Ph_2P(CH_2)_3Si(OC_2H_5)_3]_2(CO)_2$ complex. However, the 1978 $cm^{-1}$ band is very similar to that (1975 $cm^{-1}$) of the *trans* isomer of the dirhodium complex $[Rh(\mu\text{-}SC_6H_5)(PPh_3)(CO)]_2$.[15] According to the literature,[17] the product of the reaction between $Rh_2(\mu\text{-}SC_6F_5)_2(CO)_4$ and 2 equiv of $PPh_3$ at low temperature (−5 °C) is *cis*-$[Rh(\mu\text{-}SC_6F_5)(PPh_3)(CO)]_2$ ($\nu$(CO) 1994, 1977 $cm^{-1}$), but the product is *trans*-$[Rh(\mu\text{-}SC_6F_5)(PPh_3)(CO)]_2$ ($\nu$(CO) 1984 $cm^{-1}$) when the reaction is run at room temperature. Our IR experiments show that *cis*-Rh−S−P also isomerizes to *trans*-Rh−S−P upon heating in toluene at 80 °C for 40 min. So, it appears that the tethering reaction in refluxing toluene causes the *cis*-Rh−S−P complex to isomerize to *trans*-Rh−S−P.

**Hydroformylation of 1-Octene.** The hydroformylation reactions were carried out in a three-necked, jacketed vessel closed with a self-sealing silicon rubber cap; the vessel was connected to a vacuum/CO−$H_2$ line and a constant-pressure gas buret. The temperature of the ethylene glycol that circulated through the vessel jacket was maintained with a constant-temperature bath. The reaction temperature and the pressure of CO−$H_2$ (1/1) were 60 °C and 1 atm, respectively. After the catalyst and phosphorus ligand were added and the atmosphere in the vessel was replaced with CO−$H_2$, toluene and 1-octene were added by syringe with vigorous stirring and the uptake of CO−$H_2$ was followed with the constant-pressure gas buret. After the reaction was stopped, the reaction mixture was analyzed by GC. When the Rh−S/$SiO_2$ catalyst was used in three successive hydroformylations of 1-octene, the reaction mixture after the first cycle was filtered and the solid catalyst was washed with toluene, dried under vacuum, and used for the hydroformylation of a new batch of 1-octene by following the same procedure as that in the first cycle. After the second cycle, the catalyst was treated as after the first cycle; the isolated catalyst was used for the third cycle.

To determine if any of the rhodium leached from the solid catalyst, the rhodium contents of the liquid phases from the first and second cycles were analyzed by atomic emission spectroscopy. It was found that 1.5% of the total rhodium on

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**Table 1. Hydroformylation of 1-Octene over Rh−S/SiO$_2$[a]**

| P ligand | reacn time (h) | TOF[b] (min$^{-1}$) | TO[c] | conversn[d] (%) | aldehyde selectivity (%)[e] | n/i[f] | isomerizn product (%)[g] |
|---|---|---|---|---|---|---|---|
| none | 12 | 0 | 0 | 0 | | | 0 |
| P(OPh)$_3$ | 11 | 1.19 | 504 | 85.8 | 68.5 | 12.0 | 28.0 |
| P(C$_6$H$_4$F-*p*)$_3$ | 22 | 0.66 | 564 | 70.5 | 91.6 | 4.2 | 5.8 |
| PPh$_3$ | 22 | 0.39 | 415 | 51.1 | 93.9 | 4.1 | 3.1 |
| P(C$_6$H$_4$OMe-*p*)$_3$ | 23 | 0.25 | 271 | 32.5 | 95.4 | 4.5 | 1.5 |
| P(C$_6$H$_{11}$)$_3$ | 24 | 0.07 | 80 | 11.0 | 82.7 | 1.4 | 1.9 |
| PMe$_3$ | 8 | 0 | 0 | 0 | | | 0 |
| dppe[h] | 12 | 0 | 0 | 0 | | | 0 |
| dppm[h] | 21 | 0 | 0 | 0 | | | 0 |

[a] Reaction conditions: Rh−S/SiO$_2$ (50 mg, 7.26 × 10$^{-3}$ mmol of Rh), 1-octene (1.00 mL, 6.38 mmol), P/Rh = 7.8, toluene (5 mL), 60 °C, 1 atm (1/1, H$_2$−CO). [b] The maximum turnover frequency defined as moles of aldehyde formed per mole of rhodium per minute. [c] Turnover (moles of aldehyde formed per mole of rhodium) corresponds to the reaction time. [d] The conversion of 1-octene measured by GC corresponds to the reaction time. [e] Aldehyde selectivity (total yield of moles of 1-nonanal and 2-methyloctanal per mole of 1-octene converted) determined by GC. [f] Mole ratio of 1-nonanal/2-methyloctanal. [g] The yield of isomerization byproducts (total of 2-, 3-, and 4-octene) determined by GC analysis. [h] dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$; dppm = Ph$_2$PCH$_2$PPh$_2$.

the catalyst leached into the liquid phase in the first cycle. In the second cycle, 0.75% of the rhodium complex leached into the liquid phase. The liquid phases separated from the first and second cycles were also used for the hydroformylation of 1-octene under the same conditions as those used with the solid catalyst. After the first cycle (22 h), during which time 0.80 mL of 1-octene was converted, 0.80 mL of 1-octene was added to the solution phase. The hydroformylation rate (milliliters of CO and H$_2$ uptake per minute) of the solution phase was only one-sixth of that of the first cycle with the solid catalyst (Rh−S/SiO$_2$). The rate of hydroformylation of the solution phase from the second cycle was only one-seventh of that of the second cycle with the Rh−S/SiO$_2$ catalyst. Thus, less than 17% of the hydroformylation is catalyzed by the Rh that leaches into the solution. No $\nu$(CO) absorptions were detected in IR spectra of solutions after the first cycle, despite the observation that the solution showed catalytic activity.

In all experiments, the hydroformylation products were 1-nonanal and 2-methyloctanal. In most cases the only isomerization products observed were *cis*- and *trans*-2-octene. However, when the P(OPh)$_3$ cocatalyst was used, *cis*- and *trans*-3-octene and *cis*- and *trans*-4-octene were also formed. No hydrogenation products of the aldehydes or 1-octene were detected. There was no evidence for products resulting from the hydroformylation of the internal olefins 2-, 3-, and 4-octene.

## Results and Discussion

**Rh−S/SiO$_2$ as Catalyst Precursor.** The silica-tethered rhodium carbonyl thiolate catalyst Rh−S/SiO$_2$ was used for the hydroformylation of 1-octene in toluene solvent in the presence of a phosphine or phosphite donor under the conditions of 60 °C and 1 atm of H$_2$ and CO (1:1). As the data in Table 1 show, the hydroformylation rate, conversion, and selectivity for aldehyde products are strongly affected by the nature of the phosphorus ligand. Rh−S/SiO$_2$ alone is inactive for both the hydroformylation and the isomerization of 1-octene. The highest hydroformylation rate (TOF = 1.19 min$^{-1}$) was achieved when P(OPh)$_3$ was used as the cocatalyst. This TOF is about 3 or 17 times higher than those of the catalyst systems using PPh$_3$ or P(C$_6$H$_{11}$)$_3$, respectively. To our knowledge, this is the most active immobilized rhodium complex catalyst system for the hydroformylation of olefins under such mild conditions. Hydroformylations of olefins over anchored rhodium complex catalysts reported previously are generally performed under high pressure (normally ≥40 atm) of H$_2$ and CO.[18−23] In comparison to the other catalyst systems in Table 1, that involving P(OPh)$_3$ also gives the highest regioselectivity (n/i, mole ratio of 1-nonanal/2-methyloctanal), a value of 12, which is about 3 or 8 times greater than those observed with PPh$_3$ or P(C$_6$H$_{11}$)$_3$, respectively. However, with regard to the chemoselectivity for aldehyde, P(OPh)$_3$ is much worse than the phosphine ligands. While the P(OPh)$_3$ catalyst system gives a conversion of 85.7%, its selectivity for aldehyde is only 68.5% and the yield of isomerization byproducts is 28.0%. When the P(OPh)$_3$/Rh ratio was increased from 7.8 to 15, the percent of isomerization increased to 34.5% while the n/i ratio was unchanged (12.1) in a 20 h run. Decreasing the P(OPh)$_3$/Rh ratio to 3.6 affected the isomerization (32.6%) slightly, but the n/i ratio decreased to 7.7 in a 21.5 h run.

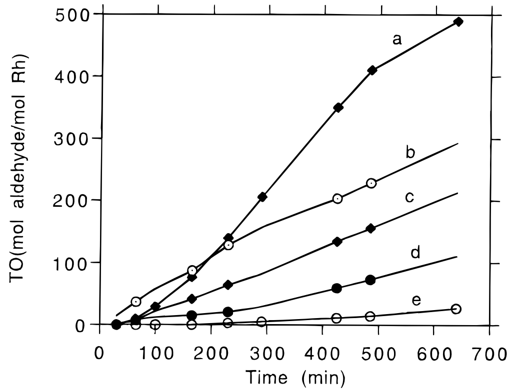

**Figure 1.** Kinetic curves for the hydroformylation of 1-octene by Rh−S/SiO$_2$ with the P-donor cocatalysts: (a) P(OPh)$_3$; (b) P(C$_6$H$_4$F-*p*)$_3$; (c) PPh$_3$; (d) P(C$_6$H$_4$OMe-*p*)$_3$; (e) P(C$_6$H$_{11}$)$_3$. For reaction conditions, see Table 1.

The arylphosphine ligands are better cocatalysts than the more basic alkylphosphines for both the hydroformylation rate and the chemo- and regioselectivities. For the three aryl phosphine ligands, the hydroformylation rates decrease in the order P(C$_6$H$_4$F-*p*)$_3$ > PPh$_3$ >P(C$_6$H$_4$OMe-*p*)$_3$, while the selectivities for aldehyde decrease in the opposite order: P(C$_6$H$_4$OMe-*p*)$_3$ > PPh$_3$

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**Table 2. Effect of $PPh_3$/Rh Mole Ratio on the Catalytic Behavior of Rh−S/$SiO_2$ in the Hydroformylation of 1-Octene[a]**

| P/Rh | reacn time (h) | TOF[b] ($min^{-1}$) | TO[c] | conversn[d] (%) | aldehyde selectivity (%)[e] | n/i[f] | isomerizn products (%)[g] |
|---|---|---|---|---|---|---|---|
| 1.3 | 22 | 0.45 | 301 | 89.6 | 38.6 | 3.0 | 55.0 |
| 2.6 | 23 | 0.95 | 720 | 98.1 | 84.1 | 3.4 | 15.6 |
| 5.2 | 12.5 | 1.25 | 673 | 85.4 | 90.4 | 3.8 | 8.2 |
| 7.8 | 22 | 0.39 | 415 | 51.1 | 93.9 | 4.1 | 3.1 |

[a] For reaction conditions, see Table 1. Footnotes are the same as in Table 1.

> $P(C_6H_4F\text{-}p)_3$. These trends demonstrate that electron-withdrawing substituents on the phenyl rings accelerate both the hydroformylation and the side reaction of isomerization. The regioselectivity (n/i) of the three arylphosphine catalyst systems is about the same. The catalyst systems Rh−S/$SiO_2$−$PMe_3$, Rh−S/$SiO_2$−dppe, and Rh−S/$SiO_2$−dppm, are inactive for the hydroformylation of 1-octene under these mild reaction conditions.

Figure 1 shows kinetic curves for the hydroformylation of 1-octene over Rh−S/$SiO_2$ with different phosphorus ligand cocatalysts. Except for Rh−S/$SiO_2$−$P(C_6H_4F\text{-}p)_3$, which is active from the outset (Figure 1b), the catalyst systems with the other phosphorus ligands exhibit an induction period. The length of the induction period decreases as the basicity of the phosphorus ligand decreases: $P(C_6H_{11})_3$ > $P(C_6H_4OMe\text{-}p)_3$ > $PPh_3$ > $P(OPh)_3$.

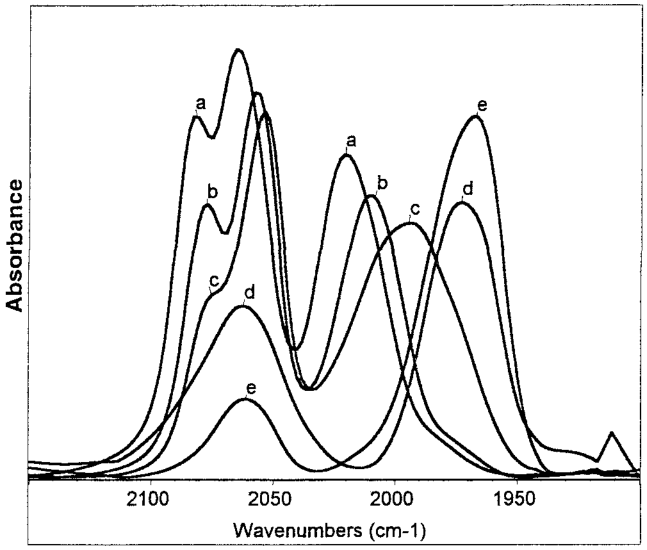
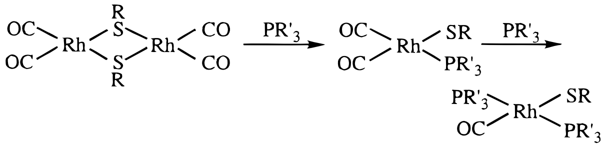


**Figure 2.** Comparison of the DRIFT spectra of the used Rh−S/$SiO_2$−$PPh_3$ catalyst with different $PPh_3$/Rh mole ratios after hydroformylations of 1-octene: (a) unreacted Rh−S/$SiO_2$; (b) P/Rh = 1.3; (c) P/Rh = 2.6; (d) P/Rh = 5.2; (e) P/Rh = 7.8.

The effect of the P/Rh ratio on the rate, conversion, and selectivity of 1-octene hydroformylation was investigated using the $PPh_3$ ligand. As the data illustrate in Table 2, the catalyst system with the highest P/Rh mole ratio gives the highest chemoselectivity for aldehydes and highest regioselectivity for the linear aldehyde. The maximum hydroformylation rate (TOF) is obtained at a P/Rh mole ratio of about 5. To gain some insight into the structures of species formed during the hydroformylation reactions, IR spectra (DRIFTS) (Figure 2) were recorded in air on the used catalysts, which were isolated at the end of the reaction time (Table 2) by filtering the catalysts from the reaction mixtures, washing with toluene, and drying under vacuum. Spectra of the isolated Rh−S/$SiO_2$−$PPh_3$ catalysts used with different $PPh_3$/Rh mole ratios are shown in Figure 2. When the mole ratio of P/Rh is 1.3, the spectrum of the used catalyst is very similar to that of the unreacted Rh−S/$SiO_2$. As the P/Rh ratio increases, the $\nu$(CO) band at around 2081 $cm^{-1}$ gradually disappears. When the P/Rh ratio reaches 5.2, the used catalyst exhibits bands at 2060 and 1975 $cm^{-1}$ with similar intensities. The positions of these bands are lower than those (2090 and 2005 $cm^{-1}$)[24] of *cis*-$RhCl(CO)_2(PPh_3)$, which is consistent with the stronger donor ability of $RS^-$ ligands[25] and suggests that the structure of the complex on the surface is of the type $Rh(SR)(CO)_2(PPh_3)$. When the P/Rh ratio is increased to 7.8, the relative intensity of the band at 2060 $cm^{-1}$ decreases substantially and a new band at 1970 $cm^{-1}$ grows in. The position of this latter band is very similar to that (1969 $cm^{-1}$) in $Rh(SCH_3)(CO)(PPh_3)_2$.[15] These spectral changes suggest that the predominant species on the surface change with increasing $PPh_3$/Rh ratio, as illustrated in eq 2. Since $Rh(SR)(CO)_2(PPh_3)$ is the predominant species present when the $PPh_3$/Rh ratio (5.2) gives the most active catalyst, it appears that a $Rh(SR)(CO)_2(PPh_3)$ type of complex, although not necessarily involved in the catalysis, is associated with the activity of the catalyst.



(2)

DRIFT spectra of isolated Rh−S/$SiO_2$ catalysts that had been used with different phosphorus ligand cocatalysts (P/Rh ratio of 7.8) for the reaction times given in Table 1 are shown in Figure 3. When no phosphorus ligand was added, the IR spectrum of the used catalyst remains the same as that of the unreacted Rh−S/$SiO_2$. The IR spectrum of the used Rh−S/$SiO_2$−dppe catalyst gives three $\nu$(CO) bands at 2080 (m), 2060 (s), and 2010 (s) $cm^{-1}$. These are very similar to those of the unreacted catalyst Rh−S/$SiO_2$, which suggests that dppe does not react nor cleave the thiolate bridge of the tethered rhodium carbonyl complex Rh−S/$SiO_2$. Both Rh−S/$SiO_2$ alone and Rh−S/$SiO_2$−dppe are inactive for the hydroformylation of 1-octene (Table 1). Spectra of the isolated catalysts using $PPh_3$, $P(OPh)_3$, $P(C_6H_4OMe\text{-}p)_3$, and $P(C_6H_4F\text{-}p)_3$ as cocatalyst show two $\nu$(CO) bands at 2055−2065 and 1965−1975 $cm^{-1}$ (Figure 3b−e). For $P(C_6H_4F\text{-}p)_3$ and $P(C_6H_4OMe\text{-}p)_3$, the intensities of the two bands are similar. However, for $PPh_3$ and $P(OPh)_3$, the 1965−1975 $cm^{-1}$ band is more intense than that of the 2055−2065 $cm^{-1}$ band. These results suggest, as discussed for the spectra of catalysts using different $PPh_3$/Rh ratios (Figure 2), that two types of complexes are present, one of the type $Rh(SR)(CO)_2(PR'_3)$ with two bands (one in each of the 2055−2065 and 1965−1975 $cm^{-1}$ regions). The other complex is of the type *trans*-

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[24] Uguagliati, P.; Deganello, G.; Belluco, U. *Inorg. Chim. Acta* **1974**, *9*, 203.

[25] Lever, A. B. P. *Inorg. Chem.* **1990**, *28*, 1271.

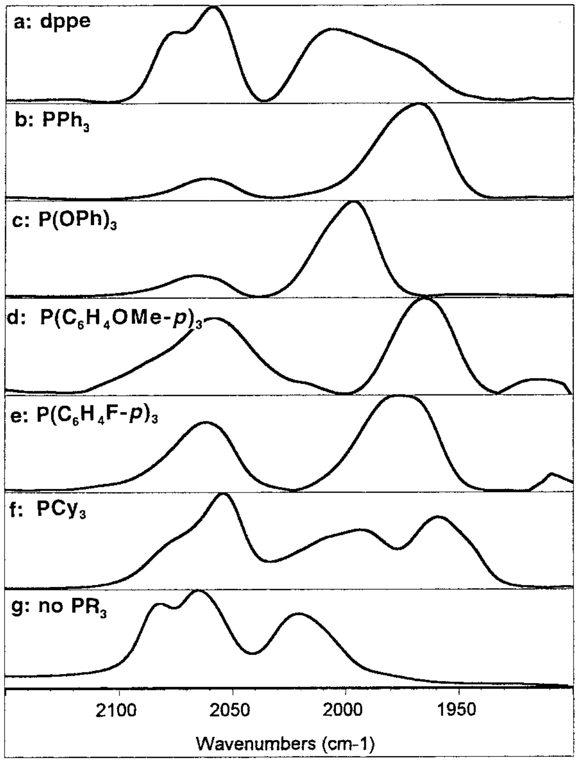

**Figure 3.** Comparison of the DRIFT spectra of the Rh−S/$SiO_2$ catalysts with different phosphorus ligands after being used in the hydroformylation of 1-octene: (a) dppe; (b) $PPh_3$; (c) $P(OPh)_3$; (d) $P(C_6H_4OMe\text{-}p)_3$; (e) $P(C_6H_4F\text{-}p)_3$; (f) $P(C_6H_{11})_3$; (g) no $PR_3$.

$Rh(SR)(CO)(PR'_3)_2$ with one band in the 1965−1975 $cm^{-1}$ region. On the basis of these $\nu$(CO) data, we conclude that in the cases of $P(C_6H_4F\text{-}p)_3$ and $P(C_6H_4\text{-}OMe\text{-}p)_3$, the major species present on the used catalyst is the mononuclear dicarbonyl complex *cis*-$Rh(SR)(CO)_2(PR'_3)$, on the basis of the fact that the two bands (2055−2065 and 1965−1975 $cm^{-1}$) are very similar to those (2060 and 1975 $cm^{-1}$) assigned to *cis*-$Rh(SR)(CO)_2(PPh_3)$ in the $PPh_3$/Rh ratio studies (Figure 2). However, for the $P(OPh)_3$ and $PPh_3$ cocatalysts, the single 1965−1975 $cm^{-1}$ band suggests that the major species formed on the used catalyst surface has a structure similar to that of $Rh(SCH_3)(CO)(PPh_3)_2$,[15] which has a band at 1969 $cm^{-1}$ as discussed above; the smaller band at 2055−2065 $cm^{-1}$ suggests that some of the $Rh(SR)(CO)_2(PR'_3)$ complex is also present. As is evident in Figure 3, the relative intensity of the $\nu$(CO) band at 2055−2065 $cm^{-1}$ increases with the phosphorus ligand in the order $PPh_3 < P(OPh)_3 < P(C_6H_4OMe\text{-}p)_3 \approx P(C_6H_4F\text{-}p)_3$, which suggests that the fraction of the dicarbonyl species $Rh(SR)(CO)_2(PR'_3)$ on the used catalyst surfaces decreases in the order $P(C_6H_4F\text{-}p)_3 \approx P(C_6H_4OMe\text{-}p)_3 > P(OPh)_3 > PPh_3$. Thus, it appears that the hydroformylation activity of the $Rh(SR)(CO)_2(PR'_3)$ species is strongly affected by the basicity of the phosphorus ligand: the weaker the basicity of the ligand, the higher the activity of the complex.

For the Rh−S/$SiO_2$−$P(C_6H_{11})_3$ catalyst system (Figure 3f), after the hydroformylation proceeds for 24 h, there is still some of the original rhodium carbonyl complex Rh−S on the catalyst surface, as indicated by the $\nu$(CO) bands at 2078 (sh), 2056 (s), and 2008 (br); the additional bands at 2054 and 1954 $cm^{-1}$ (the band at 2056 $cm^{-1}$ overlaps with that of the unreacted rhodium complex Rh−S) indicate the presence of some $Rh(SR)(CO)_2(PR'_3)$. It seems that there is no rhodium complex species of the type $Rh(SR)(CO)(P(C_6H_{11})_3)_2$ on the used catalyst surface. This indicates that it is more difficult for the larger $P(C_6H_{11})_3$ ligand to react with Rh−S/$SiO_2$, compared to the other monophosphine ligands. The used catalyst isolated from the Rh−S/$SiO_2$−$PMe_3$ catalyst system does not show any detectable $\nu$(CO) bands in its DRIFT spectrum. All of these results suggest that the structure of the rhodium species on the $SiO_2$ surface after hydroformylation is sensitive to the phosphorus ligand used.

**Table 3. Effect of $PPh_3$/Rh Mole Ratio on the Catalytic Behavior of Rh−S−P/$SiO_2$ in the Hydroformylation of 1-Octene[a]**

| P/Rh | reacn time (h) | TOF[b] ($min^{-1}$) | TO[c] | conversn[d] (%) | aldehyde selectivity (%)[e] | n/i[f] | isomerizn products (%)[g] |
|---|---|---|---|---|---|---|---|
| none | 18.5 | 0 | 0 | 13.3 | 0 | | 13.3 |
| 1.6 | 24.0 | 0.33 | 370 | 97.5 | 71.4 | 3.4 | 27.9 |
| 3.2 | 24.0 | 0.35 | 470 | 98.2 | 89.8 | 3.4 | 10.0 |
| 7.4 | 21.0 | 0.49 | 499 | 98.2 | 95.2 | 4.2 | 4.7 |
| 10 | 25.0 | 0.46 | 492 | 97.9 | 94.1 | 4.6 | 5.8 |

[a] Reaction conditions are the same as those in Table 1. Footnotes are the same as in Table 1.

**Rh−S−P/$SiO_2$ as Catalyst Precursor.** The hydroformylation reactions catalyzed by Rh−S/$SiO_2$ required the addition of a phosphorus donor cocatalyst. In principle, it seemed possible that the phosphine cocatalyst could also be anchored to the support. Thus, the complex $Rh_2[\mu\text{-}S(CH_2)_3Si(OCH_3)_3]_2[Ph_2P(CH_2)_3Si(OC_2H_5)_3]_2(CO)_2$ (Rh−S−P), with anchoring siloxy groups on both the thiolate and phosphine ligands, was tethered to the $SiO_2$ to give the Rh−S−P/$SiO_2$ catalyst, which was used to catalyze the hydroformylation of 1-octene at 60 °C and 1 atm of CO−$H_2$. It was observed (Table 3) that, as for Rh−S/$SiO_2$, Rh−S−P/$SiO_2$ alone is inactive for the hydroformylation of 1-octene under these mild conditions, although it exhibits a low activity for the isomerization of 1-octene. Thus, anchoring both the sulfur and phosphine ligands in Rh−S−P/$SiO_2$ does not give an active hydroformylation catalyst. However, Rh−S−P/$SiO_2$ is active for hydroformylation in the presence of added $PPh_3$ (Table 3). With an increase in the $PPh_3$/Rh mole ratio, the hydroformylation rate (TOF and TO), aldehyde selectivity, and 1-nonanal/2-methyloctanal (n/i) mole ratio increase. When $PPh_3$/Rh is 7.4, the hydroformylation rate and the regio- and chemoselectivity reach a maximum but decline only slightly when the $PPh_3$/Rh mole ratio is increased to 10. Figure 4 shows the IR (DRIFT) spectra of the isolated Rh−S−P/$SiO_2$−$PPh_3$ catalysts that had been used with different $PPh_3$/Rh mole ratios at the end of the reaction times in Table 3. When $PPh_3$ was not added to the reaction mixture, the spectrum of the used catalyst showed three $\nu$(CO) bands at 2078 (m), 2060 (s), and 2011 (s) $cm^{-1}$, which are within experimental error the same as those of the Rh−S/$SiO_2$ catalyst. This result indicates that the phosphine in the tethered Rh−S−P complex is replaced by CO to give tethered Rh−S in the absence of $PPh_3$ under the hydroformylation conditions. As for the Rh−S/$SiO_2$ catalyst, the $\nu$(CO) band at 2078 $cm^{-1}$ disappears with an increase in the $PPh_3$/Rh mole ratio. When a $PPh_3$/Rh mole ratio of 7.4 is achieved, the used

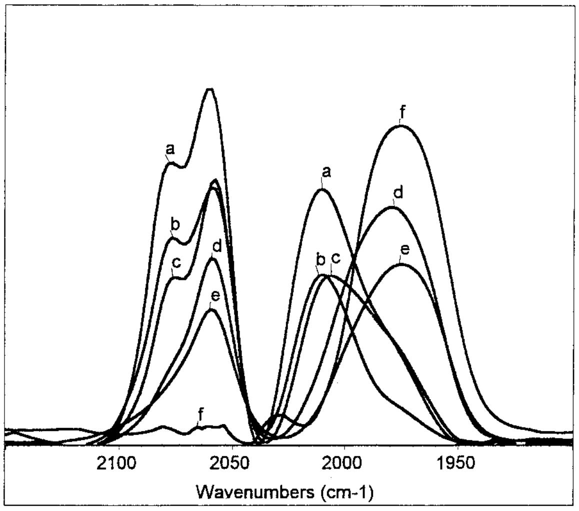

**Figure 4.** Comparison of the DRIFT spectra of the used Rh−S−P/$SiO_2$−$PPh_3$ catalyst with different $PPh_3$/Rh mole ratios after hydroformylations of 1-octene: (a) no $PPh_3$; (b) P/Rh = 1.6; (c) P/Rh = 3.2; (d) P/Rh = 7.4; (e) P/Rh = 10; (f) unreacted Rh−S−P/$SiO_2$.

catalyst exhibits two $\nu$(CO) bands, at 2058 and 1975 $cm^{-1}$, with similar intensities. The positions and relative intensities of these bands are similar to those (Figure 2) of the used Rh−S/$SiO_2$−$PPh_3$ with a $PPh_3$/Rh mole ratio of approximately 5. Thus, the Rh−S−P/$SiO_2$−$PPh_3$ catalyst is largely converted to the Rh−S/$SiO_2$−$PPh_3$ catalyst under the conditions of hydroformylation. Also, the conversions of the tethered Rh−S−P complex with increasing $PPh_3$ concentration follow the pattern (eq 2) observed for the tethered Rh−S complex. In both cases, a $Rh(SR)(CO)_2(PPh_3)$ species is the major complex on the surface at a $PPh_3$/Rh ratio (5−7) that gives a maximum hydroformylation activity.

In a further attempt to generate a hydroformylation catalyst in which both the rhodium complex and phosphine cocatalyst were tethered to the $SiO_2$, we first tethered $Ph_2P(CH_2)_3Si(OC_2H_5)_3$ to $SiO_2$ by reacting 0.64 mmol of the ligand with $SiO_2$ (0.8 g) in refluxing toluene for 4 h. The resulting P−$SiO_2$ solid was treated with the Rh−S complex in toluene at room temperature for 2 h to form the Rh−S/P−$SiO_2$ (Rh, 1.7 wt %) catalyst. The IR (DRIFT) spectrum of this catalyst, which shows three $\nu$(CO) bands at 2056 (s), 1995 (s), and 1975 (s) $cm^{-1}$, is clearly different from those of Rh−S (2074 (m), 2056 (s), 2004 (s) $cm^{-1}$), Rh−S−P (1970 (s), 1956 (s) $cm^{-1}$) or Rh−S−P/$SiO_2$ (1978 $cm^{-1}$); however, they are similar to those (2050 (s), 1990 (s), and 1972 (s) $cm^{-1}$ in hexadecane) of $[Rh(\mu\text{-S-}t\text{-}C_4H_9)(CO)_2(PMe_2Ph)]_2$,[26] in which the Rh centers are 5-coordinate. This suggests that the major species on the Rh−S/P−$SiO_2$ catalyst is the five-coordinate rhodium thiolate complex $Rh_2[\mu\text{-}S(CH_2)_3Si(OCH_3)_3]_2[Ph_2P(CH_2)_3Si(OC_2H_5)_3]_2(CO)_4$. In hydroformylation studies using the conditions in Table 1, Rh-S/P−$SiO_2$ alone is unfortunately inactive for the hydroformylation of 1-octene; however, it is active in the presence of $PPh_3$. After Rh−S/P−$SiO_2$ was used for the hydroformylation of 1-octene for 24 h, the DRIFT spectrum of the isolated catalyst showed that when no $PPh_3$ was added, the $\nu$(CO) bands remained the same as those of the unreacted Rh−S/P−$SiO_2$; however, when $PPh_3$ was added at a $PPh_3$/Rh mole ratio of 6, the isolated catalyst showed two $\nu$(CO) bands at 2054 (s) and 1978 (s) $cm^{-1}$. The positions and intensities of these bands are very similar to those (2055−2065 and 1965−1975 $cm^{-1}$) that were assigned to a $Rh(SR)(CO)_2(PR'_3)$ species in the Rh−S/$SiO_2$−$PR'_3$ and Rh−S−P/$SiO_2$−$PPh_3$ catalyst systems, which suggests that the same type of species is generated in the Rh−S/P−$SiO_2$−$PPh_3$ system.

Although several reports on the homogeneous hydroformylation of alkenes catalyzed by $[Rh(\mu\text{-}SR)(CO)(PR'_3)]_2$ indicate that the dinuclear rhodium catalyst precursors maintain their integrity throughout the catalytic cycle,[8,9,13] recent kinetic evidence[27] strongly suggests that a mononuclear complex is involved. Spectroscopic studies show, however, that $Rh_2(\mu\text{-}SR)_2(CO)_2(PR'_3)_2$ complexes are the predominant species observed during the homogeneous hydroformylation of olefins.[28] We also used the homogeneous catalyst Rh−S/$PPh_3$ to catalyze the hydroformylation of 1-octene under the same conditions as in Table 1. The results show that when the $PPh_3$/Rh mole ratio is 5, the maximum TOF and the TO during a 24 h period are 0.26 and 275, respectively, which are lower than those (1.25 and 673 (in 12.5 h), 0.49 and 499 (in 21 h)) obtained using the Rh−S/$SiO_2$−$PPh_3$ ($PPh_3$/Rh = 5.2) and Rh−S−P/$SiO_2$−$PPh_3$ ($PPh_3$/Rh = 7.4) catalyst systems. The IR spectrum of the hydroformylation solution exhibits two $\nu$(CO) bands at 1973 (s) and 1965 (s) $cm^{-1}$, which are similar to those (1966 (s) and 1952 (s) $cm^{-1}$ in hexadecane) of *cis*-$[Rh(S\text{-}t\text{-}C_4H_9)(CO)(PMe_2Ph)]_2$;[26] this suggests that the rhodium complex species formed in the homogeneous hydroformylation reaction is *cis*-$Rh_2[\mu\text{-}S(CH_2)_3Si(OCH_3)_3]_2(PPh_3)_2(CO)_2$, analogous to the $[Rh(\mu\text{-}SR)(CO)(PR'_3)]_2$ system.[8,9,13] It is clear that the predominant species present in the homogeneous Rh−S/$PPh_3$ catalyst system is different from that ($Rh(SR)(CO)_2(PR'_3)$) in the tethered catalyst systems, Rh−S/$SiO_2$−$PPh_3$ and Rh−S−P/$SiO_2$−$PPh_3$. Thus, the tethering of Rh−S to $SiO_2$ stabilizes the complex in different forms ($Rh(SR)(CO)_2(PR'_3)$ and $Rh(SR)(CO)(PR'_3)_2$) than what exists in the homogeneous catalyst system ($Rh_2(\mu\text{-}SR)_2(CO)_2(PR'_3)_2$). This stabilization of $Rh(SR)(CO)_2(PR'_3)$ by $SiO_2$ attachment may be the reason for the higher activity of the Rh−S/$SiO_2$−$PR'_3$ and Rh−S−P/$SiO_2$−$PPh_3$ catalyst systems as compared with the homogeneous Rh−S/$PPh_3$ catalyst system.

Finally, the durability of the Rh−S/$SiO_2$−$PPh_3$ catalyst with a $PPh_3$/Rh ratio of 7.8 was evaluated in three successive hydroformylations of 1-octene under the conditions in Table 1. In the first cycle, the maximum TOF was 0.39 and the TO was 415 after 22 h. Then, the catalyst was filtered from the mixture, washed with toluene, and dried under vacuum at room temperature. It was observed that in the second hydroformylation cycle the addition of $PPh_3$ is still essential for the reaction. Using the same $PPh_3$/Rh mole ratio as in the first cycle, this catalyst system gave a maximum TOF of 0.30 and a TO value of 307 after 21.5 h. After the catalyst was treated as described after the first cycle, it was used in a third cycle for which the maximum TOF

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was 0.49 and the TO was 551 after 25.5 h. Thus, during the third cycle, the catalyst had essentially the same TO activity as in the first cycle. For the three cycles over 69 h, the total turnover number was 1273 mol of aldehyde/mol of Rh. The DRIFT spectrum of the used catalyst after the third cycle is about the same as that of the used catalyst in the first cycle ($\nu$(CO) at 2060 (w) and 1970 (s) $cm^{-1}$), even though excess $PPh_3$ ($PPh_3$/Rh = 7.8) was added to the reaction solution for each cycle.

## Summary

The silica-tethered rhodium thiolate complex catalysts, Rh−S/$SiO_2$ and Rh−S−P/$SiO_2$, discussed in this paper are very active for the hydroformylation of 1-octene in the presence of a phosphine cocatalyst under the mild conditions of 60 °C and 1 atm. The hydroformylation rate (TOF and TO), conversion, and chemo- and regioselectivity for aldehyde products are markedly affected by the phosphine donor and the mole ratio of P/Rh. The high activity of the tethered catalysts may result from the stabilization of a monorhodium dicarbonyl thiolate type of complex, $Rh(SR)(CO)_2(PR'_3)$, which is the predominant species on the most active form of the catalysts using $PPh_3$ as cocatalyst. These tethered catalysts are easy to separate from the reaction mixture and exhibit good durability for the hydroformylation of 1-octene. Attempts to tether both Rh−S and the phosphine cocatalyst on the $SiO_2$ did not give a catalyst that was active for hydroformylation, unless another phosphine cocatalyst was added to the solution.

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