

Unmodified Rhodium-Catalyzed Hydroformylation of Alkenes Using Tetra­rhodium Dodecacarbonyl. The Infrared Characterization of 15 Acyl Rhodium Tetracarbonyl Intermediates[†]

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The homogeneous catalytic hydroformylation of 20 alkenes was studied, starting with $\text{Rh}_4(\text{CO})_{12}$ as catalyst precursor in *n*-hexane as solvent, using high-pressure in-situ infrared spectroscopy as the analytical tool. Five categories of alkenes were studied, namely, cycloalkenes (cyclopentene, cycloheptene, cyclooctene, and norbornene), symmetric internal linear alkenes (3-hexene, 4-octene, and 5-decene), terminal alkenes (1-hexene, 1-octene, 1-decene, 1-dodecene, and 1-tetradecene), methylene cycloalkanes (methylene cyclopropane, methylene cyclobutane, methylene cyclopentane, and methylene cyclohexane), and branched alkenes (2-methyl-2-butene, 2-methyl-2-pentene, 2-methyl-2-heptene, and 2,3-dimethyl-2-butene). The typical reaction conditions were $T = 293 \text{ K}$, $P_{\text{H}_2} = 2.0 \text{ MPa}$ (0.018 mol fraction), $P_{\text{CO}} = 2.0 \text{ MPa}$ (0.033 mol fraction), $[\text{alkene}]_0 = 0.1\text{--}0.02 \text{ mol fraction}$, and $[\text{Rh}_4(\text{CO})_{12}]_0 = 6.6 \times 10^{-5} \text{ mol fraction}$. In each experiment, with the exception of those involving methylene cyclopropane and the branched alkenes, the precursor $\text{Rh}_4(\text{CO})_{12}$ was converted in good yield to the corresponding observable mononuclear acyl rhodium tetracarbonyl intermediate $\text{RCORh}(\text{CO})_4$. Due to the spectral characteristics, the intermediate $\text{RCORh}(\text{CO})_4$ is assigned a trigonal bipyramidal geometry in all cases with C_s symmetry, with the acyl group taking an axial position. Under the present conditions, the cycloalkenes result in one acyl complex, the symmetric internal linear alkenes result in two acyl stereoisomers, the terminal alkenes result in three acyl complexes (two are stereoisomers), and the methylene cycloalkanes result in two acyl complexes. The first four categories of alkenes gave rise to slightly different spectral wavenumbers and relative intensities for the complexes, namely, cycloalkenes {2109 (0.41), 2063 (0.46), 2037 (0.72), 2019 (1.0), 1699 cm^{-1} (0.16)}, symmetric internal linear alkenes {2108 (0.43), 2061 (0.45), 2037 (0.84), 2019 (1.0), 1693 cm^{-1} (0.12)}, terminal alkenes {2110 (0.35), 2064 (0.46), 2038 (0.72), 2020 (1.0), 1703 cm^{-1} (0.16)}, and methylene cycloalkanes {2110 (0.33), 2064 (0.46), 2038 (0.72), 2020 (1.0), 1704 cm^{-1} (0.24)}. Finally, the approximate turnover frequencies (TOF) for each system were also calculated. It was found that the TOFs vary from 0.04 to 0.11 min^{-1} between alkene categories. Thus, to a first approximation, the primary differences in rates of hydroformylation are due to the conversion of $\text{Rh}_4(\text{CO})_{12}$ and not TOFs. This answers a long-standing question concerning hydroformylation rates.

Introduction

The unmodified homogeneous rhodium-catalyzed hydroformylation of alkenes has a rather long history. Some of the most pivotal developments have included the first patents, which appeared in the late 1950s,¹ the first syntheses/discoveries of the rhodium carbonyls $\text{HRh}(\text{CO})_4$,² $\text{Rh}_2(\text{CO})_8$,³ $\text{Rh}_4(\text{CO})_{12}$,⁴ and $\text{Rh}_6(\text{CO})_{16}$,⁵ the

extensive catalytic and kinetic work performed by the group at Veszprém,⁶ the discovery of $[\text{Rh}(\text{CO})_2(\mu\text{-O}_2\text{-CR})_2]$ from a sample of the hydroformylation reaction,⁷ Chini's famous stoichiometric hydroformylations of pro-

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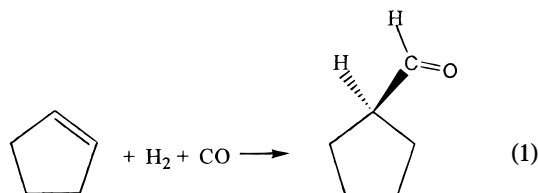
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pylene using $\text{Rh}_4(\text{CO})_{12}$ under hydrogen to give the aldehydes and $\text{Rh}_6(\text{CO})_{16}$,⁸ and the H_2/D_2 scrambling experiments of Pino and Consiglio using $\text{Rh}_4(\text{CO})_{12}$ under catalytic conditions.⁹ The overall stoichiometry of the hydroformylation reaction is illustrated by eq 1, where cyclopentene is the substrate.

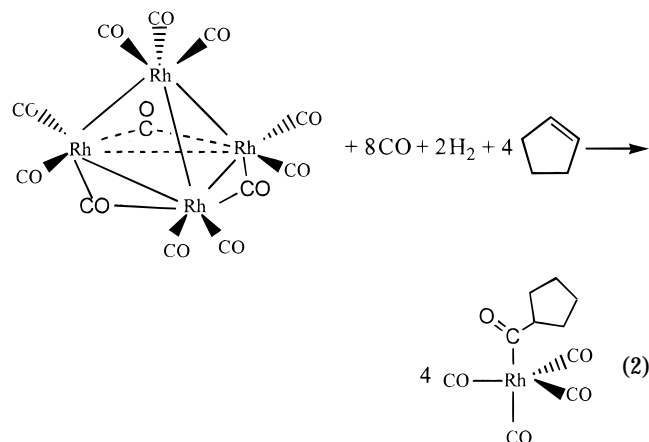


These early results clearly indicated some of the particularly troublesome problems present in studies of the unmodified rhodium-catalyzed hydroformylation reaction. One problem was the extraordinarily rapid interconversion of rhodium carbonyl species under syngas. Thus sampling of the reaction mixtures usually indicated $\text{Rh}_4(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$ as the only rhodium species present. A second problem was the extreme sensitivity of the unmodified rhodium-catalyzed hydroformylation to diene and alkyne impurities.¹⁰ A third problem was the sensitivity of the syntheses to trace oxygen and water. Clusterification, particularly to $\text{Rh}_6(\text{CO})_{16}$, readily occurred, and system deactivation was the result.¹¹ Taken together, these problems affected the reproducibility of rhodium hydroformylation kinetics and made analyses very difficult.

Despite all these complications, a viable mechanistic explanation developed. This mechanism suggested the involvement of only mononuclear rhodium intermediates in the transformation of alkenes to aldehydes, a simple unicyclic reaction topology, and the existence of a mononuclear acyl species as the predominant intermediate. The strongest support for this assertion came from Marko's kinetic experiments with cyclohexene, where it was shown that the activity was proportional to $[\text{Rh}_4(\text{CO})_{12}]^{0.25}$ and $[\text{Rh}_6(\text{CO})_{16}]^{0.17}$,^{6d} Bor's identification of $[\text{Rh}(\text{CO})_2(\mu\text{-O}_2\text{-CR})]_2$,⁷ and the similarities in H_2/D_2 scrambling between rhodium and cobalt hydroformylation systems.⁹ The Veszprém group also showed the interesting result that the reactivity of the systems followed a reproducible systematic trend, namely, styrene > terminal alkenes > internal alkenes > cyclic alkenes.

In addition, it can be noted that the unmodified rhodium-catalyzed hydroformylation exhibited two very nice features compared to the unmodified cobalt-catalyzed hydroformylation. These features were the strong suppression of hydrogenation products and the strong suppression of $\text{C}=\text{C}$ bond isomerization, particularly under mild reaction conditions.¹² Both of these properties allow potentially more straightforward kinetic analyses.

Over the past decade, numerous in-situ infrared spectroscopic and kinetic studies of the unmodified homogeneous rhodium-catalyzed hydroformylation of alkenes have been performed. These studies have focused on a number of issues. These have included (i) the extension of quantitative in-situ measurements to the ppm level under high pressure,¹³ (ii) the identification of the observable intermediate acyl rhodium tetracarbonyl during the syntheses¹⁴ [also see eq 2], (iii)



quantifying the activity of the systems in terms of the instantaneous turnover frequencies based on the concentrations of intermediates and thereby separating induction, deactivation, and product formation kinetics,¹⁵ (iv) the identification of equilibrium precursor conversion as a serious issue concerning metal utilization,^{15b} (v) statistical treatments of turnover frequencies and studies of the large variance in such kinetic measurements,¹⁶ (vi) in-situ spectroscopic and kinetics investigations of heterometallic clusters and inorganic precursors in the rhodium-catalyzed hydroformylation,¹⁷ (vii) the detailed kinetic analysis of the regioselective hydroformylation of styrene,^{15c} and (viii) statistical tests aimed to resolve the possible existence and contribution of a catalytic binuclear elimination reaction.¹⁸ With the aforementioned issues addressed, we have shifted our attention to a few remaining outstanding issues. In particular, we have been concerned with the chemistry associated with deactivation, especially with regard to the use of alkynes and dienes.¹⁹

In the present contribution we address issues surrounding the formation of the acyl rhodium tetracarbonyl intermediate in hydroformylation reactions and the approximate comparative turnover frequencies. In other words, is the acyl rhodium tetracarbonyl the only observable intermediate for all major categories of alkene hydroformylations, and is the relative reactivity

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of alkenes due to turnover effects or due to systematic changes in the conversion of the rhodium precursor?

Experimental Section

General Information. All solution preparations were carried out under argon (99.999% Pan Gas AG, Luzern, Switzerland) using standard Schlenk techniques.²⁰ The argon was further purified prior to use by passage through a column containing 100 g of reduced BTS-catalyst (Fluka AG Buchs, Switzerland) and 100 g of 4 Å molecular sieves to adsorb trace oxygen and water, respectively. All reactions were carried out under carbon monoxide (99.997% Messner Griesheim GmbH, Germany) and hydrogen (99.999% Pan Gas AG, Luzern, Switzerland) after further purification through deoxy and zeolite columns.

The precious metal complex $\text{Rh}_4(\text{CO})_{12}$, with stated purity of 98% min was obtained from Strem Chemicals SA (Bischheim, France) and was used without further purification, although trace quantities of the high nuclearity cluster $\text{Rh}_6(\text{CO})_{16}$ are virtually always present. The complex $\text{Rh}_4(\text{CO})_{12}$ is known to be oxygen, water, and light sensitive.⁴ The *n*-hexane solvent (stated purity >99.6%, Fluka AG) was refluxed over sodium potassium alloy under argon. Weights were measured with a precision of 0.1 mg. Volumes were measured with a precision of 0.045 mL. Further microanalytic techniques were not employed.²¹ All alkenes used in this study were of the highest quality commercially obtainable, usually 99.0+% (obtained either from Wiley Organic Chemicals, Lancaster Chemicals, U.K., Fluka AG, Switzerland, or Merck, Germany). Concerning further purification, the alkenes were simply degassed before use.

Equipment. In-situ spectroscopic studies were performed in a 1.5 L stainless steel (SS316) autoclave (Büchi-Uster, Switzerland), which was connected to a high-pressure infrared cell. The autoclave ($P_{\text{max}} = 22.5$ MPa) was equipped with a packed magnetic stirrer with six-bladed turbines in both the gas and liquid phases (Autoclave Engineers, Erie, PA) and was constructed with a heating/cooling mantle. A high-pressure membrane pump (Model DMK 30, Orlita AG, Geissen, Germany) with a maximum rating of 32.5 MPa and a 3 L/h flow rate was used to circulate the *n*-hexane solutions from the autoclave to the high-pressure IR cell and back to the autoclave via jacketed 1/8 in. (SS316) high-pressure tubing (Autoclave Engineers). The entire system, autoclave, transfer lines, and infrared cell, was cooled using a Lauda cryostat Model RX20 and could be maintained isothermal ($\Delta T \leq 0.5$ °C) at 298–313 °C. Temperature measurements were made at the cryostat, autoclave, and IR cell with PT-100 thermoresistors. The necessary connections to vacuum and gases were made with 1/4 in. (SS316) high-pressure tubing (Autoclave Engineers), and 1.0, 5.0, and 10.0 piezocrystals were used for pressure measurements (Keller AG Winterthur, Switzerland). The entire system was gastight under vacuum as well as at 20.0 MPa, the maximum operating pressure.

The high-pressure infrared cell was constructed at the ETH-Zürich of SS316 steel and could be heated and cooled. The CaF_2 single-crystal windows (Korth Monokristalle, Kiel, Germany) had dimensions of 40 mm diameter by 15 mm thickness. Two sets of Viton and silicone gaskets provided sealing, and Teflon spacers were used between the windows. The construction of the flow-through cell²² is a variation on a design due to Noack²³ and differs in some respects from other high-pressure infrared

cells described in the literature (for a review, see Whyman²⁴). The high-pressure cell was situated in a Perkin-Elmer 983 infrared spectrometer. The resolution was set to 4 cm^{-1} for all spectroscopic measurements. A schematic diagram of the experimental setup can be found in ref 15c.

In-Situ Spectroscopic and Kinetic Studies. The experiments were performed in a similar manner. First, single-beam background spectra of the IR sample chamber were recorded. Then 5–20 mL of alkene was dissolved in 150 mL of *n*-hexane, and this solution was transferred under argon to the autoclave. Under 0.2 MPa CO pressure, infrared spectra of the alkene solution in the high-pressure cell were recorded. The total system pressure was raised to 2.0 MPa CO, and the stirrer and high-pressure membrane pump were started. After equilibration, infrared spectra of the alkene/*n*-hexane/CO solution in the high-pressure cell were recorded. A solution of 100 mg of $\text{Rh}_4(\text{CO})_{12}$ dissolved in 100 mL of *n*-hexane was prepared, transferred to the high-pressure reservoir under argon, pressured with CO, and then added to the autoclave. Infrared spectra of the alkene/*n*-hexane/CO/ $\text{Rh}_4(\text{CO})_{12}$ solution in the high-pressure cell were recorded. Hydrogen (2.0 MPa) was then added to initiate the syntheses. Spectra were recorded at 15 min intervals in the range 1600–2200 and 1100–1300 cm^{-1} .

A considerable number of spectral subtractions were performed on each reaction spectrum in order to subtract the absorbance of the *n*-hexane solvent, dissolved CO, the absorbance of the $\text{Rh}_4(\text{CO})_{12}$, the absorbance of the alkenes, and the absorbance of the aldehydes.

The solubility of CO under these reaction conditions was approximately 0.033 mole fraction, and the solubility of H_2 was approximately 0.018 mole fraction.¹⁷ Consequently, the moles in each experiment were 1.51 mol of *n*-hexane, 0.05 mol of CO, and 0.03 mol of H_2 . Since the amount of $\text{Rh}_4(\text{CO})_{12}$ used in the experiments was ca. 100 mg, and since the maximum amount of alkenes was ca. 20 mL, the corresponding in-situ measured initial concentrations of $\text{Rh}_4(\text{CO})_{12}$ in the experiments was ca. 6.6×10^{-5} mole fraction.

The present hydroformylation reactions were performed under negligible gas–liquid mass transfer resistance. The experimentally measured overall mass transfer coefficients K_{1a} for hydrogen and carbon monoxide into *n*-hexane at 200 rpm were approximately 0.1 and 0.6 s^{-1} , respectively, as determined using the method of Deimling.²⁵ Since the maximum observed rate of hydroformylation in this study was $4 \times 10^{-7} \text{ mol s}^{-1}$, all experiments belong to the category of infinitely slow reaction with respect to gas–liquid mass transfer (i.e., the kinetic regime, Hatta category H).²⁶ The liquid phase of each experiment became essentially saturated with dissolved CO and H_2 in the first 60 s. Mass transfer effects are known to severely complicate the interpretation of kinetic data from hydroformylation reactions.²⁷

In any single 8 h kinetic experiment, less than 0.01 mol conversion (or 3%) of alkene to aldehyde occurred. Therefore, the partial pressures of hydrogen and carbon monoxide in the closed-batch autoclave changed less than 1% during the each 8 h experiment. This partial pressure change was considered negligible, and hence, the liquid-phase concentrations of the two gaseous components were treated as constants for the duration of each experiment.

The approximate mole fractions of the acyl rhodium tetracarbonyl species $\text{RCORh}(\text{CO})_4$ and the aldehydes were deter-

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mined by measuring the absorbance at 2020 cm^{-1} and at the aldehyde maximum, and by using the absorptivity $2500\text{ L}/(\text{mol cm})$ at 2020 cm^{-1} , the absorptivity $375\text{ L}/(\text{mol cm})$ for aldehydes, and the absorptivity $1.95\text{ L}/(\text{mole cm})$ at 1138 cm^{-1} for hexane. Calculations were made using the dimensionless Lambert–Beer law (eq 3).²⁸ The term x_{C_6} is the mole fraction of *n*-hexane at the initial reaction conditions.

$$x_i = x_{\text{C}_6}(A_{i,1138})/(A_{1138}\epsilon_i) \quad (3)$$

The rates of reaction for the transformation of alkenes to aldehydes were calculated from the concentrations using a central difference approximation. The central difference approximation was chosen since it provides an accurate approximation of derivatives from sets of smooth monotonically increasing or decreasing experimental data.²⁹ In addition, extensive investigations concerning the numerical evaluation of turnover frequencies in homogeneous catalytic systems support the central difference approximation.¹⁶ Turnover frequencies were calculated using the formula

$$\text{TOF}_t = \frac{\Delta[\text{aldehyde}]_t}{[\text{acyl}]_t \Delta t} \quad (4)$$

Results

Cycloalkenes. Four cycloalkenes were used in these experiments: cyclopentene, cycloheptene, cyclooctene, and norbornene. The first three cyclic alkenes result in only one aldehyde each, namely, cyclopentane carboxaldehyde, cycloheptane carboxaldehyde, and cyclooctane carboxaldehyde. Therefore, only one acyl intermediate is expected in the corresponding hydroformylation experiments. However, these aldehydes occur in more than one conformation; for example, in the case of cyclohexane carboxaldehyde, both the chair and boat conformations exist. In the case of norbornene, two different product isomers occur, namely, the *endo* and *exo* configurations. Consequently, in these hydroformylations, two acyl isomers also occur.

Only ca. 50% conversion of the precursor $\text{Rh}_4(\text{CO})_{12}$ was observed in the first 8 h of the hydroformylation experiments. The mid-infrared spectrum of each acyl product is shown in Figure 1. It is immediately seen that the acyl rhodium tetracarbonyls have very similar spectral characteristics, namely, four terminal CO's and one "organic" CO vibration near 1699 cm^{-1} . In these spectra, the presence of $\text{Rh}_6(\text{CO})_{16}$ can be observed in both the cycloheptene spectrum and the cyclooctene spectrum at 2073 cm^{-1} . In addition a very weak band can be observed at ca. 1990 cm^{-1} in all spectra.

The region between 2200 and 2100 cm^{-1} is noisy due to the subtraction of dissolved CO. In the spectrum of the cyclooctene-derived acyl, a sigmoid waveform is seen at 1885 cm^{-1} after subtraction of the reference $\text{Rh}_4(\text{CO})_{12}$. Finally, the "organic" CO vibration is symmetric—indicating only one isomer—at least in the cases of cyclopentene, cycloheptene, and cyclooctene. The resulting aldehyde bands were symmetric and occurred at ca. 1732.8 cm^{-1} , and the width at half-height (WHH) was about 12 cm^{-1} . It is noted that this WHH is slightly

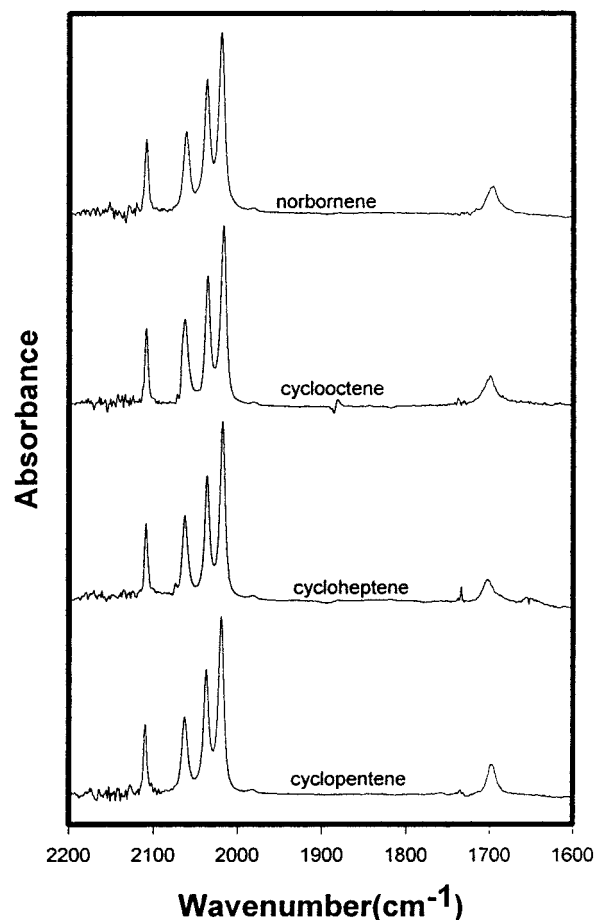


Figure 1. Mid-infrared spectra of acyl rhodium tetracarbonyl complexes derived from cyclic alkenes after subtraction of $\text{Rh}_4(\text{CO})_{12}$, hexane, CO, alkene, and aldehyde.

Table 1. Relative Infrared Absorbance of Acyl Rhodium Tetracarbonyls Derived from Cyclic Alkenes

alkene	$\nu_{\text{CO}} (\text{cm}^{-1})$ above, relative intensity below				$\nu_{\text{CO}} (\text{cm}^{-1})$
cyclopentene	2109.9	2063.1	2037.3	2019.6	1698.2
	0.40	0.44	0.70	1	0.18
cycloheptene	2109.0	2063.0	2036.5	2018.1	1703.2
	0.42	0.47	0.69	1	0.13
cyclooctene	2108.8	2063.2	2036.0	2017.1	1699.3
	0.42	0.47	0.72	1	0.16
norbornene	2108.6	2061.8	2037.1	2019.8	1696.4
	0.40	0.45	0.74	1	0.17

larger than normal. This is probably due to the numerous conformations possible.

The detailed spectroscopic characteristics of the acyl complexes are given in Table 1. The average wavenumbers for the all acyl complexes in this category were 2109 (0.41), 2063 (0.46), 2037 (0.72), 2019 (1.0), and 1699 cm^{-1} (0.16), where the relative intensities are given in parentheses. It is clear from numerical data that the spectroscopic characteristics are very similar for each acyl complex in both the terminal CO region and the "organic" CO region.

The measured approximate turnover frequencies for the four systems were as follows: TOF cyclopentene = 0.06 min^{-1} , TOF cycloheptene = 0.10 min^{-1} , TOF cyclooctene = 0.20 min^{-1} , and TOF norbornene = 0.07 min^{-1} . Thus, the average TOF for cyclic alkenes was ca. 0.11 min^{-1} .

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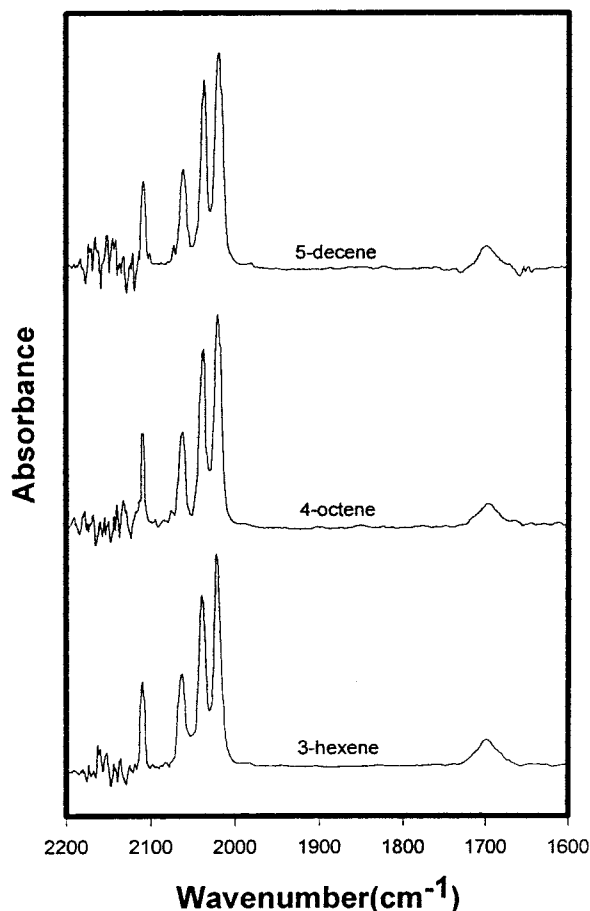


Figure 2. Mid-infrared spectra of acyl rhodium complexes derived from symmetric internal linear alkenes after subtraction of $\text{Rh}_4(\text{CO})_{12}$, hexane, CO, alkene, and aldehyde.

Symmetric Internal Linear Alkenes. Three alkenes were used in these experiments: 3-hexene, 4-octene, and 5-decene.³⁰ These alkenes result in two aldehydes each, namely, *rac*-2-ethylpentanal, *rac*-2-*n*-propylhexanal, and *rac*-2-*n*-butylheptanal. Therefore, two stereoisomeric acyl rhodium tetracarbonyl intermediates are produced in each of the corresponding hydroformylation experiments. However, using unpolarized infrared radiation, each pair of racemic aldehydes and each pair of racemic acyl complexes have exactly the same infrared absorbance spectrum.

Again, only ca. 50% conversion of the precursor $\text{Rh}_4(\text{CO})_{12}$ was observed in the first 8 h of the hydroformylation experiments. The mid-infrared spectrum of each acyl product is shown in Figure 2. [Please note that the uneven quality of this figure is due to the redigitalization of the data from hardcopies.] It is immediately seen that the three racemic acyl rhodium tetracarbonyls have very similar spectral characteristics, namely, four terminal CO's and one "organic" CO vibration near 1693 cm^{-1} . In these spectra, the presence of $\text{Rh}_6(\text{CO})_{16}$ can be observed in both the 4-octene and 5-decene spectra at 2073 cm^{-1} . In addition the very weak band at ca. 1990 cm^{-1} is again observed in all spectra, and the region between 2200 and 2100 cm^{-1} is particularly noisy due to the subtraction of dissolved CO. Finally, the "organic" CO band is symmetric, indicating exact superposition of the isomers. The resulting aldehyde bands were

Table 2. Relative Infrared Absorbance of Acyl Rhodium Tetracarbonyls Derived from Symmetric Internal Linear Alkenes

alkene	ν_{CO} (cm^{-1}) above, relative intensity below				ν_{CO} (cm^{-1})
	2108.9	2062.3	2037.3	2019.2	
3-hexene	0.41	0.45	0.81	1	0.13
4-octene	0.45	0.45	0.83	1	0.12
5-decene	0.41	0.46	0.87	1	0.12

symmetric and occurred at ca. 1732.0 cm^{-1} , and the width at half-height (WHH) was only 10 cm^{-1} .

The average frequencies for the resulting acyl complexes were 2108 (0.43), 2061 (0.45), 2037 (0.84), 2019 (1.0), and 1693 cm^{-1} (0.12), where the relative intensities are given in parentheses. Detailed spectroscopic characteristics are given in Table 2. It is clear from the numerical data that the spectroscopic characteristics are very similar for each acyl complex.

The measured approximate turnover frequencies for the three systems were as follows: TOF 3-hexene = 0.05 min^{-1} , TOF 4-octene = 0.07 min^{-1} , and TOF 5-decene = 0.11 min^{-1} . Thus, the average TOF for symmetric linear alkenes was ca. 0.08 min^{-1} .

Terminal Linear Alkenes. Five alkenes were used in these experiments: 1-hexene, 1-octene, 1-decene, 1-dodecene, and 1-tetradecene. Each of these alkenes results in three aldehydes. For example, in the case of 1-hexene, the expected products are 1-heptanal and *rac*-2-methylhexanal.

The reactivity of the rhodium precursor $\text{Rh}_4(\text{CO})_{12}$ toward these terminal alkenes was much greater than that observed for the aforementioned internal alkenes. In the present series of experiments, nearly 100% conversion of the precursor $\text{Rh}_4(\text{CO})_{12}$ was observed in the first 8 h of the hydroformylation experiments. The mid-infrared spectrum of each set of acyl products is shown in Figure 3. It is seen that all the acyl rhodium tetracarbonyls have very similar spectral characteristics, namely, the four terminal CO's and one "organic" CO vibration. In these spectra, the presence of $\text{Rh}_6(\text{CO})_{16}$ can be observed in all cases due to the bands present at both 2073 and 1820 cm^{-1} . Again a very weak band at ca. 1990 cm^{-1} is observed in all spectra, and the region between 2200 and 2100 cm^{-1} is noisy due to the subtraction of dissolved CO. The "organic" CO vibration is clearly seen at ca. 1703 cm^{-1} for all alkenes, 1-hexene, 1-octene, 1-decene, 1-dodecene, and 1-tetradecene, and the "organic" CO vibration is clearly asymmetric (the asymmetry is certainly not an artifact of the spectral subtractions). This indicates that the primary maximum at 1703 cm^{-1} is due to coordination at the α carbon atom, and the relatively weak sideband at 1694 is due to coordination at the β carbon atom. Therefore we observe all three possible acyl isomers. The resulting aldehyde bands were visibly asymmetric, at least in the cases of 1-decene, 1-dodecene, and 1-tetradecene. This indicates the formation of both the linear and branched aldehydes in observable quantities. The typical aldehyde band had a center at ca. 1734.8 cm^{-1} and a width at half-height (WHH) of about 14 cm^{-1} . This very broad WHH is further confirmation of the presence of both linear and branched aldehydes under these reaction conditions.

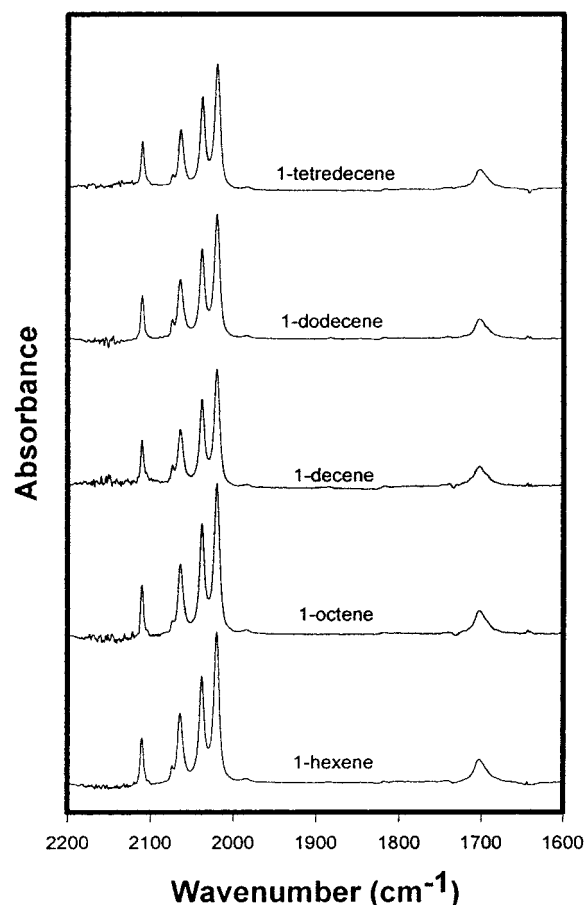


Figure 3. Mid-infrared spectra of acyl rhodium complexes derived from terminal linear alkenes after subtraction of hexane, CO, alkene, and aldehyde.

Table 3. Relative Infrared Absorbance of Acyl Rhodium Tetracarbonyls Derived from Terminal Linear Alkenes

alkene	ν_{CO} (cm^{-1}) above, relative intensity below				ν_{CO} (cm^{-1})
1-hexene	2110.5	2064.2	2038.2	2020.2	1702.9
	0.33	0.45	0.70	1	0.15
1-octene	2110.5	2064.1	2038.0	2020.0	1703.1
	0.34	0.47	0.72	1	0.16
1-decene	2110.6	2064.5	2038.4	2020.4	1703.2
	0.36	0.48	0.73	1	0.16
1-dodecene	2110.3	2064.3	2038.0	2020.2	1702.7
	0.38	0.47	0.69	1	0.16
1-tetradecene	2110.7	2064.2	2038.0	2020.1	1702.8
	0.35	0.46	0.73	1	0.16

The average wavenumbers for the resulting mixtures of acyl complexes were 2110 (0.35), 2064 (0.46), 2038 (0.72), 2020 (1.0), and 1703 cm^{-1} (0.16), where the relative intensities are given in parentheses. The detailed spectroscopic characteristics are given in Table 3. It is clear from the numerical data that the spectroscopic characteristics are very similar for the acyl complexes.

The measured approximate turnover frequencies for the five systems were as follows: TOF 1-hexene = 0.01 min^{-1} , TOF 1-octene = 0.11 min^{-1} , TOF 1-decene = 0.05 min^{-1} , TOF 1-dodecene = 0.05 min^{-1} and TOF 1-tetradecene = 0.05 min^{-1} . Thus, the average TOF for the terminal alkenes was ca. 0.05 min^{-1} .

Methylene Cycloalkanes. Four methylene cycloalkanes were used in these experiments: methylene

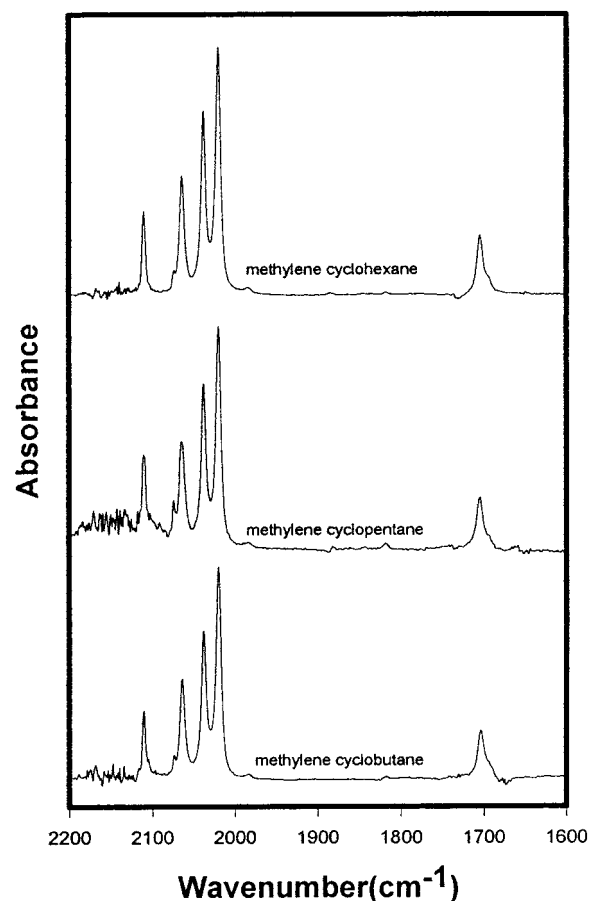


Figure 4. Mid-infrared spectra of acyl rhodium complexes derived from methylene cycloalkanes after subtraction of hexane, CO, alkene, and aldehyde.

cyclopropane, methylene cyclobutane, methylene cyclopentane, and methylene cyclohexane. In the latter three cases, hydroformylation readily occurred. Unusual chemistry occurred only in the case of methylene cyclopropane as substrate. In principle, each of the hydroformylated alkenes could result in two aldehydes each. For example, in the case of methylene cyclobutane, the expected products are 2-cyclobutyl ethanal and 1-formyl-1-methylcyclobutane.

Again, the reactivity of the rhodium precursor $\text{Rh}_4(\text{CO})_{12}$ toward the methylene cycloalkanes was much greater than that toward the internal alkenes. In the present series of experiments, nearly 100% conversion of the precursor $\text{Rh}_4(\text{CO})_{12}$ was observed in the first 8 h of the hydroformylation experiments. The mid-infrared spectrum of each set of acyl products is shown in Figure 4. It is seen that all the sets of acyl rhodium tetracarbonyls have very similar spectral characteristics, namely, the four terminal CO's and one "organic" CO vibration. In these spectra, the presence of $\text{Rh}_6(\text{CO})_{16}$ can be observed in all cases due to the bands present at both 2073 and 1820 cm^{-1} . Again a very weak band at ca. 1990 cm^{-1} is observed in all spectra, and the region between 2200 and 2100 cm^{-1} is noisy due to the subtraction of dissolved CO. Finally, the "organic" CO vibration is clearly seen at ca. 1704 cm^{-1} , and in the case of all three alkenes, the "organic" CO vibration is clearly asymmetric. This indicates that the primary maximum at 1704 cm^{-1} is due to coordination at the α carbon atom, and the moderate sideband at 1696 cm^{-1}

Table 4. Relative Infrared Absorbance of Acyl Rhodium Tetracarbonyls Derived from Methylene Cycloalkanes

alkene	ν_{CO} (cm ⁻¹) above, relative intensity below				ν_{CO} (cm ⁻¹)
methylene	2109.9	2064.3	2038.3	2020.4	1703.8
cyclobutane	0.31	0.47	0.70	1	0.23
methylene	2110.7	2064.8	2038.2	2020.1	1704.0
cyclopentane	0.33	0.45	0.73	1	0.25
methylene	2110.3	2063.9	2037.8	2020.2	1704.5
cyclohexane	0.36	0.47	0.73	1	0.24

is due to coordination at the β carbon atom. Therefore we observe both possible acyl complexes. The resulting aldehyde bands were visibly asymmetric, particularly in the case of methylene cyclohexane. The latter aldehyde had a maximum at 1733.5 cm⁻¹, a strong shoulder at 1730 cm⁻¹, and a width at half-height (WHH) of about 13 cm⁻¹.

The average frequencies for the resulting mixtures of acyl complexes were 2110 (0.33), 2064 (0.46), 2038 (0.72), 2020 (1.0), and 1704 (0.24), where the relative intensities are given in parentheses. The detailed spectroscopic characteristics are given in Table 4. It is clear from the numerical data that the spectroscopic characteristics are very similar for each of the acyl complexes.

The measured approximate turnover frequencies for the 3 systems were as follows: TOF methylene cyclobutane = 0.04 min⁻¹, TOF methylene cyclopentane = 0.04 min⁻¹, and TOF methylene cyclohexane = 0.04 min⁻¹. Thus, the average TOF for methylene cycloalkanes was ca. 0.04 min⁻¹.

Results with Methylene Cyclopropane. The reaction of methylene cyclopropane with Rh₄(CO)₁₂ under hydroformylation conditions gave unexpected results. Five different experiments were performed at 20 °C with 250 mL of *n*-hexane solvent, 5 mL of methylene cyclopropane, and 100 mg of Rh₄(CO)₁₂. The partial pressures of CO and H₂ used were 0.5 MPa/1.0 MPa, 1.0 MPa/1.0 MPa, 2.0 MPa/1.0 MPa, 2.0 MPa/2.0 MPa, and 4.0 MPa/1.0 MPa. In each of the five experiments, essentially the same infrared spectra at 2200–1950 cm⁻¹ were generated under reaction conditions. This region is very complex and contains at least 15 predominant bands. Figure 5 shows spectra from three experiments as well as a typical deconvolution.

Interestingly, there is a relatively weak band at ca. 1703 cm⁻¹, which suggests an acyl complex, and a very weak band at 1733 cm⁻¹, indicative of the formation of a small amount of the linear aldehyde. However, there are not any bands at ca. 1695 nor 1730 cm⁻¹. Together, these results strongly suggest that a rhodium carbonyl hydride can successfully attack the α carbon atom and form an acyl complex. However, it appears that attack at the β carbon atom results in ring opening. Ring opening of the cyclopropane moiety would result in a host of new reaction products. Indeed, the ring opening of cyclopropanes is well documented, and rhodium complexes are particularly suitable for this purpose.³¹ In the present context it can be noted that rhodium

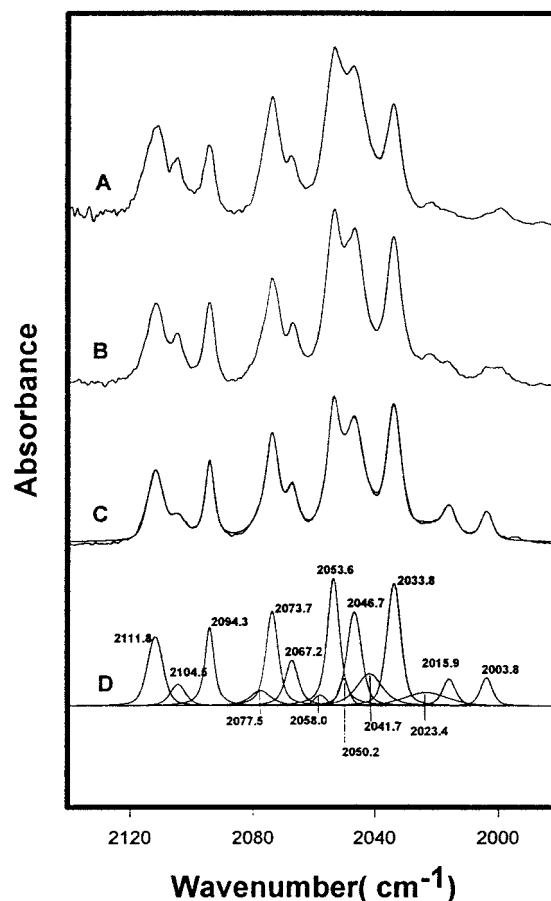


Figure 5. Mid-infrared spectra of the reaction of Rh₄(CO)₁₂ with methylene cyclopropane under hydroformylation conditions: (A) 4.0 MPa CO, 1.0 MPa H₂, (B) 2.0 MPa CO and 1.0 MPa H₂, (C) 1.0 MPa CO and 1.0 MPa H₂ with best curve fit, (D) deconvolution of spectra.

carbonyl complexes have been successfully used to break cyclopropane structures.³² Finally, we note that there is considerable similarity in the terminal CO region of the present experiment and hydroformylations performed with dienes.^{19b} Indeed, if the methylene cyclopropane structure is destroyed at the β carbon atom, followed by hydrogen migration, one obtains 1,3-butadiene. This issue will be treated in more detail elsewhere.^{19b}

Branched Alkenes. The hydroformylations of the following branched alkenes were also attempted: 2-methyl-2-butene, 2-methyl-2-pentene, 2-methyl-2-heptene, and 2,3-dimethylbut-2-ene. Most of these experiments showed negligible conversion of the precursor Rh₄(CO)₁₂ and usually little or no product. Thus, it seems that the present reaction conditions are not optimal for observing intermediates.

Discussion

Acyl Rhodium Tetracarbonyls. Previous to this study, five acyl rhodium tetracarbonyls formed from 3,3-dimethylbut-1-ene, cyclohexene, and styrene were spectroscopically characterized. In all cases, four terminal CO vibrations and one "organic" CO vibration were observed.^{13,14,15b,c,17}

In the present spectral results, from the first four categories of alkenes (and with the exception of meth-

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ylene cyclopropane), only one type of rhodium intermediate was ever observed. In all cases, only the acyl rhodium tetracarbonyl could be identified, and no other unusual spectral features were present. All the acyl rhodium tetracarbonyls possessed four strong terminal CO vibrations (and a small overtone at ca. 1990 cm^{-1}) and one "organic" CO vibration. No bridging CO ligands were observed. All the spectral data are consistent with only one type of geometry, namely, a trigonal bipyramid mononuclear species with an axial acyl group and with C_s symmetry. As Bor has pointed out on many occasions, the introduction of the acyl moiety causes a loss of C_{3v} symmetry in many mononuclear transition metal complexes.³³ The strong vibration at ca. 2108–2110 cm^{-1} , which belongs to the totally symmetric in-phase stretching mode, is indicative of the low symmetry of this mononuclear species.³⁴

The small vibration that appears at ca. 1990 cm^{-1} is almost certainly due to the ^{13}C O-substituted isotopomers. Indeed, this band has ca. 1% of the integral absorbance of the most prominent terminal CO vibration, which appears at ca. 2020 cm^{-1} . These data are consistent with the natural abundance of 1.1% ^{13}C and a shift to lower wavenumbers of up to 45 cm^{-1} .³⁵

A correlation could be found between the highest cm^{-1} vibrations of the acyl complexes and the category of alkene used. In the cases of the cycloalkenes and the symmetric internal linear alkenes, the highest vibration occurred at 2108–2109 cm^{-1} , and in the cases of terminal alkenes and methylene cycloalkanes, the highest vibration occurred at 2110–2111 cm^{-1} .

The "organic" CO vibration is also clearly correlated with the nature of the adjacent carbon atom in the acyl structure. Accordingly, for the terminal alkenes and the methylene cycloalkanes, the primary acyl structure was one in which the α carbon atom had been attacked and the resulting adjacent carbon atom was a primary carbon atom. This consistently gave a wavenumber of 1703–1704 cm^{-1} . In the case of the internal alkenes, namely, the cycloalkenes and the symmetric linear alkenes, attack occurred exclusively at a secondary carbon atom. These acyl structures consistently gave a wavenumber of 1694–1696 cm^{-1} .

As a final note in this regard, it is well-known that the vibrations of the CO moiety in aldehydes correlate with the type of carbon atom adjacent to the carbonyl group. Thus, in the case of a primary adjacent carbon atom, the carbonyl vibration is found at ca. 1738 cm^{-1} ,³⁶ in the case of a secondary adjacent carbon atom the carbonyl vibration is found at ca. 1729 cm^{-1} ,³⁷ and in the case of a tertiary adjacent carbon atom the carbonyl

vibration is found at ca. 1715 cm^{-1} .³⁷ All three were measured in CCl_4 solvent.

Turnover Frequencies. As mentioned in the Introduction, Marko et al. found a clear correlation between the category of alkenes used in a hydroformylation and the rate of aldehyde formation: styrene > terminal > internal > branched > cyclic at ca. 70 °C. In the present study, we found that the turnover frequencies follow the trend cyclic alkenes > symmetric linear alkenes > terminal alkenes > methylene cycloalkanes at 20 °C. However, the TOF varied only a little from 0.04 to 0.11. We also found that the degree of conversion of $\text{Rh}_4(\text{CO})_{12}$ followed the trend terminal alkenes \approx methylene cycloalkanes > cyclic alkenes \approx symmetric linear alkenes > branched alkenes. Thus, *it seems that TOF is not the primary controlling factor for the rates of aldehyde formation.* Instead, it seems that the *degree of precursor conversion and hence the amount of acyl complex formed* is the most important factor with regard to the rates of product formation between categories of alkenes.

Other Intermediates. The present contribution indicates that the acyl rhodium tetracarbonyl is the only observable rhodium intermediate in hydroformylation experiments conducted with four major categories of unsubstituted simple alkenes. One final important category of alkenes remains to be explored, namely, ethylene and substituted ethylenes. In these experiments, a new rhodium species is observed. This issue will be taken up further in a later contribution.³⁸

Conclusions

The in-situ infrared spectroscopic results from five categories of alkenes showed only one observable rhodium intermediate during unmodified homogeneous hydroformylations. This acyl rhodium tetracarbonyl was consistently present in the active hydroformylation experiments, and its mid infrared spectral pattern was very similar between categories of alkenes. All acyl rhodium tetracarbonyl intermediates observed in this study have trigonal bipyramid geometry, with C_s symmetry and the acyl group in the axial position. As a generalization, it appears that under most reactions conditions, and using simple alkenes or simple aliphatic-substituted alkenes, the acyl rhodium tetracarbonyl complex is by far the predominant intermediate present in solution. This implies that CO insertion is very rapid and the possibility of observing an alkyl rhodium tetracarbonyl is remote.

The approximate turnover frequencies for these systems were also evaluated. It was found that the TOFs do not vary much. Between categories of alkenes, TOFs of 0.04–0.11 min^{-1} were measured. The higher TOFs were observed for the acyl complexes formed at secondary carbon atoms, and the lower TOFs were observed for acyl complexes formed at primary carbon atoms. In addition it was observed that the conversion of the precursor $\text{Rh}_4(\text{CO})_{12}$ was lower for the former and higher for the latter systems. This strongly implies that the acyl complexes formed from secondary carbon atoms have a higher free energy than the acyl complexes formed from primary carbon atoms. In other words the acyl complexes formed at primary carbon atoms are thermodynamically more stable.

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