

# Homogeneous Hydroformylation of Ethylene Catalyzed by $\text{Rh}_4(\text{CO})_{12}$ . The Application of BTEM to Identify a New Class of Rhodium Carbonyl Spectra: $\text{RCORh}(\text{CO})_3(\pi\text{-C}_2\text{H}_4)$

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**Summary:** The homogeneous rhodium-catalyzed hydroformylation of ethylene was studied, starting with  $\text{Rh}_4(\text{CO})_{12}$  in *n*-hexane solvent. The organometallic intermediates and the organic products were measured under isobaric and isothermal conditions using in situ high-pressure infrared spectroscopy. The newly developed algorithm of band-target entropy minimization (BTEM) was applied for the spectral reconstruction to the semibatch data. The classic acyl complex  $\text{RCORh}(\text{CO})_4$  was observed, as well as a new metal carbonyl spectrum. Aldehyde and ketone were observed as organic products. The new organometallic spectrum possesses an acyl band and three strong terminal carbonyl vibrations. The new spectrum was most pronounced at very high ethylene concentrations. Although some very minor vibrations are also apparent, the spectrum is consistent with a trigonal bipyramid structure  $\text{RCORh}(\text{CO})_3\text{L}$  ( $\text{L} = \text{C}_2\text{H}_4$ ). Given the presence of the ketone formed and the small vibrational intensity at ca.  $1725\text{ cm}^{-1}$  in the new spectrum, the presence of some observable  $\text{RCOCH}_2\text{CH}_2\text{Rh}(\text{CO})_3\text{L}$  ( $\text{L} = \text{C}_2\text{H}_4$ ) cannot be excluded.

## Introduction

An extraordinary wide range of alkenes have been hydroformylated.<sup>1</sup> Although linear (terminal and internal) and cyclic alkenes have been the focus of most studies, more unusual structures such as methylene cycloalkanes and various highly functionalized alkenes have also been studied. In most of these investigations, hydroformylation to the corresponding aldehyde is by far the predominant overall organic transformation, particularly when rhodium is used. Competitive hydrogenation to alkanes is normally an extremely minor side reaction.<sup>2</sup> The simplest alkene, ethylene, is one of the few noticeable exceptions to the general rule.

Ethylene is known to hydroformylate rapidly in the presence of unmodified rhodium complexes; however, ketone and even polyketone formation is usually negligible.<sup>3</sup> Ethylene appears to be rather unusual in

its ability to insert into an acyl–rhodium bond, thereby leading to ketone/polyketone formation. Such repeated alternating insertions of ethylene and CO have been observed with cobalt and ruthenium carbonyl complexes as catalyst precursors as well,<sup>3,4</sup> and the most productive system presently known is palladium catalyzed.<sup>5</sup>

In situ FTIR studies of the hydroformylation of ethylene starting with unmodified rhodium carbonyl species have been reported by at least two groups.<sup>6</sup> In situ FTIR studies have been seriously hindered by the fact that the spectrum of dissolved ethylene changes dramatically as partial pressure is increased. A new polymer matrix method was recently applied to rhodium-catalyzed ethylene hydroformylation. A new species was observed and assigned the stoichiometry  $\text{RCORh}(\text{CO})_3(\pi\text{-C}_2\text{H}_4)$ .<sup>7</sup>

The acyl rhodium tetracarbonyl  $\text{RCORh}(\text{CO})_4$  has been observed during active hydroformylations of a large number of alkene substrates.<sup>8</sup> This information has been used repeatedly to develop rate expressions for aldehyde formation.<sup>9</sup> With the exception of two substrates, notably methylene cyclopropane and ethylene, only the rhodium-containing precursors,  $\text{Rh}_6(\text{CO})_{16}$  and  $\text{RCORh}(\text{CO})_4$ , could be identified during syntheses. Methylene cyclopropane hydroformylation leads to complex in situ spectra, and ethylene hydroformylations exhibit a spectral pattern containing at least one new rhodium carbonyl species.

In the present contribution, a semibatch in situ study of ethylene hydroformylation is performed. The new spectral processing program BTEM<sup>10</sup> is used to recover the pure component spectra of all observable species and their concentrations. BTEM is able to overcome the problematic ethylene spectral features and to recover a

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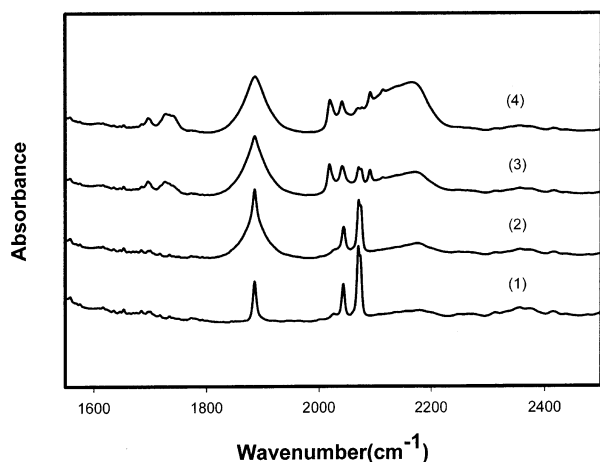
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**Figure 1.** Four in situ high-pressure FTIR spectra of the active hydroformylation semibatch reaction. The initial conditions were 298.0 mg of  $\text{Rh}_4(\text{CO})_{12}$  and 200 mL of hexane at 20.5 °C. Spectrum 1: 5 bar ethylene, 4.5 bar CO, 3.5 bar  $\text{H}_2$ . Spectrum 2: 15 bar ethylene, 4.5 bar CO, 3.5 bar  $\text{H}_2$ . Spectrum 3: 30 bar ethylene, 4.5 bar CO, 3.5 bar  $\text{H}_2$ . Spectrum 4: 30 bar ethylene, 15 bar CO, 15 bar  $\text{H}_2$ .

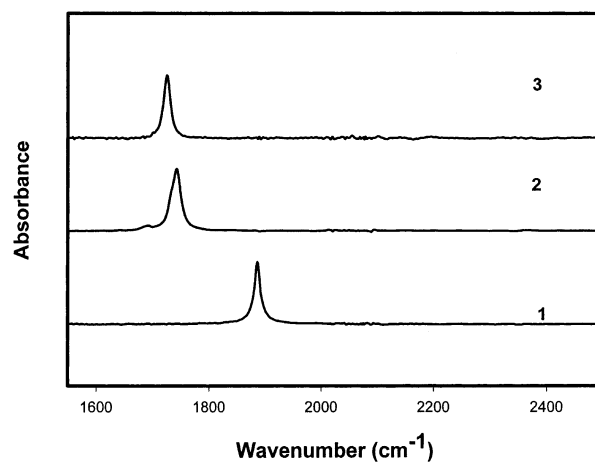
relatively clean pure component spectrum of the new class of rhodium carbonyl complexes  $\text{RCORh}(\text{CO})_3\text{L}$  ( $\text{L}$  = alkene) under real reaction conditions. The present results help to clarify the preliminary experimental results obtained by this group,<sup>6b</sup> provide further detail about the BTEM analysis of this system,<sup>6c</sup> and are consistent with the polymer matrix results recently reported by Poliakoff et al.<sup>7</sup>

## Results and Discussion

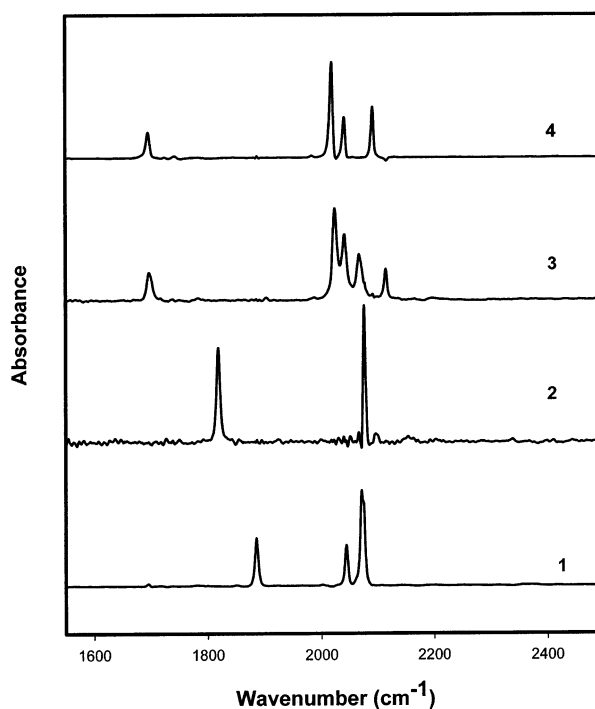
**Reaction Spectra and Spectral Distortions.** Two semibatch ethylene hydroformylations were performed at ca. 9 and 20 °C starting with  $\text{Rh}_4(\text{CO})_{12}$  as catalyst precursor. The maximum partial pressure of ethylene used was 50 bar. The problematic spectral features of ethylene are shown in Figure 1 where four in situ spectra at different reaction conditions are presented. At low partial pressures, i.e., 5 bar, ethylene has a reasonably narrow bandwidth for the band at  $1885\text{ cm}^{-1}$  (possibly overtone from  $\text{C}=\text{C}-\text{H}$  bending mode). However, as indicated by the figure, the width at half-height for ethylene can increase to ca.  $80\text{ cm}^{-1}$  at 30 bar ethylene partial pressure.

**BTEM.** The first semibatch experiment contained 6 steps/perturbation in reactants or solvent, and the second contained 8 steps. The total number of spectra taken was 366. Eleven pure component spectra were recovered by BTEM from the raw experimental spectra. These include the atmospheric moisture and  $\text{CO}_2$ , the solvent hexane, and dissolved CO, as well as three organic solutes and four organometallics.

The three organic pure component spectra were ethylene (1), propanal (2), and ketone/polyketone (3). Their pure component spectra are shown in Figure 2. The maximum for the recovered ethylene spectrum is at  $1885.8\text{ cm}^{-1}$ . It was obtained using 50 right singular



**Figure 2.** BTEM spectra of recovered organic species. Spectrum 1: ethylene. Spectrum 2: propanal. Spectrum 3: ketone/polyketone.



**Figure 3.** BTEM spectra of recovered organometallic species. Spectrum 1:  $\text{Rh}_4(\text{CO})_{12}$ . Spectrum 2:  $\text{Rh}_6(\text{CO})_{16}$ . Spectrum 3:  $\text{RCORh}(\text{CO})_4$ . Spectrum 4: new species.

vectors in the optimization and targeting the region  $1883\text{--}1887\text{ cm}^{-1}$ . This maximum is coincident with the bridging carbonyl of  $\text{Rh}_4(\text{CO})_{12}$ . The maximum absorbance of aldehyde occurs at  $1742.4\text{ cm}^{-1}$  with a shoulder at  $1693.2\text{ cm}^{-1}$ . A total of 25 vectors were used, and the region targeted was  $1741\text{--}1745\text{ cm}^{-1}$ . The maximum absorbance of the ketone/polyketone is  $1725.2\text{ cm}^{-1}$  with a shoulder at  $1701\text{ cm}^{-1}$ . A total of 25 vectors were used, and the region targeted was  $1723\text{--}1727\text{ cm}^{-1}$ . The BTEM reconstructions of the organic species show very few spectral artifacts.

The four pure component organometallic spectra recovered included the three expected spectra  $\text{Rh}_4(\text{CO})_{12}$  (1),  $\text{Rh}_6(\text{CO})_{16}$  (2), and  $\text{RCORh}(\text{CO})_4$  (3) as well as one new spectrum (4). The four organometallic spectra are shown in Figure 3. The primary vibrational features in the  $\text{Rh}_4(\text{CO})_{12}$  spectrum are  $1885.4$ ,  $2044.2$ ,  $2071.2$ , and

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2074.4  $\text{cm}^{-1}$ . A total of 25 vectors were used, and the region targeted was 2069–2073  $\text{cm}^{-1}$ . The maxima in the  $\text{Rh}_6(\text{CO})_{16}$  spectrum are 1818.4 and 2075.4  $\text{cm}^{-1}$ , obtained using 100 vectors, and the region targeted was 1816–1820  $\text{cm}^{-1}$ . The maxima in the acyl rhodium tetracarbonyl  $\text{RCORh}(\text{CO})_4$  ( $\text{R} = -\text{CH}_2\text{CH}_3$ ) spectrum are 1696.6, 2023.2, 2040.6, 2066.6, and 2113.6  $\text{cm}^{-1}$ , obtained using 50 vectors, and the region targeted was 2112–2115  $\text{cm}^{-1}$ . The maxima in the new complex are 1695.2, 2017.6, 2040.2, and 2090.4  $\text{cm}^{-1}$ , obtained using 50 vectors, and the region targeted was 2017–2019  $\text{cm}^{-1}$ .

The BTEM reconstructions of the first three complexes are very consistent with our previous studies, and the spectra show few artifacts. The relatively high levels of noise in the reconstructions of  $\text{Rh}_6(\text{CO})_{16}$  and  $\text{RCORh}(\text{CO})_4$  are due to the extremely low concentration of the former due to its solubility and the unusually low conversion to acyl in the case of ethylene hydroformylation. Higher concentrations of  $\text{RCORh}(\text{CO})_4$  have been observed using  $\text{Rh}_4(\text{CO})_{12}$  and most other alkenes.

**$\text{RCORh}(\text{CO})_3(\pi\text{-C}_2\text{H}_4)$**  The new spectrum shows a distinct artifact at 2114.4  $\text{cm}^{-1}$  due to residual mixed-in signals from  $\text{RCORh}(\text{CO})_4$ , but the signal-to-noise ratio is quite good. Three minor absorptions are apparent at 1724.2, 1741.4, and 1886.6  $\text{cm}^{-1}$ . The last two are certainly due to residual mixed-in signals from propanal and  $\text{Rh}_4(\text{CO})_{12}$  and/or ethylene.

It would appear that the band at 1695.2  $\text{cm}^{-1}$ , which is almost exactly coincident with the acyl band of  $\text{RCORh}(\text{CO})_4$ , must in fact belong to a  $\text{C}=\text{O}$  in a  $\text{RCO}$  group. This together with the simplicity of the spectrum suggests it is mononuclear. This implies that the new species is an  $\text{RCORh}(\text{CO})_x\text{L}_y$  ( $x < 4$ ,  $y \geq 1$ ). Furthermore, given the low  $C_s$  symmetry of such a species, the number of terminal vibrations will equal the number of terminal CO ligands present. Therefore the stoichiometry reduces to  $\text{RCORh}(\text{CO})_3\text{L}$ .

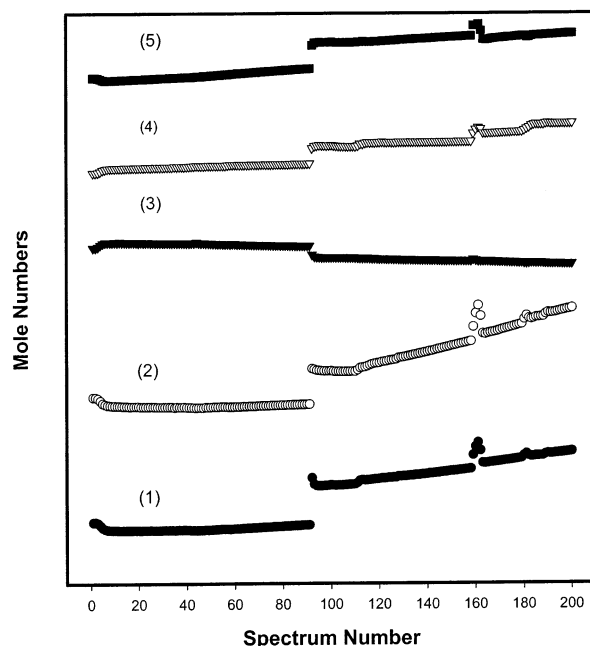
To test this hypothesis a little further, we integrated the areas under the terminal CO regions and the acyl bands. The ratio  $R$  is 4/2.7. This indicates again that  $x = 3$ .

$$R = \frac{\int_{2010}^{2120} \hat{a}_{\text{RCORh}(\text{CO})_4} / \int_{1680}^{1710} \hat{a}_{\text{RCORh}(\text{CO})_4}}{\int_{2010}^{2120} \hat{a}_{\text{RCORh}(\text{CO})_3\text{L}} / \int_{1680}^{1710} \hat{a}_{\text{RCORh}(\text{CO})_3\text{L}}} \quad (1)$$

The most obvious ligand  $\text{L}$  is  $\pi$ -coordinated ethylene. Indeed, the formation of  $\text{RCORh}(\text{CO})_3(\pi\text{-C}_2\text{H}_4)$  would be promoted by higher ethylene concentrations and lower CO concentrations. Furthermore, the insertion of the ethylene ligand into the acyl rhodium bond in  $\text{RCORh}(\text{CO})_3(\pi\text{-C}_2\text{H}_4)$ , followed by hydrogen activation, provides a mechanistic reason for the observed ketone/polyketone in the system.

Due to the presence of organic ketone in the system and due to the very minor vibration at 1724.2  $\text{cm}^{-1}$  in the reconstructed spectrum of  $\text{RCORh}(\text{CO})_3(\pi\text{-C}_2\text{H}_4)$ , the presence of a minute but observable level of  $\text{RCOCH}_2\text{-CH}_2\text{Rh}(\text{CO})_3(\pi\text{-C}_2\text{H}_4)$  cannot be excluded.

**Mole Fractions and Further Stoichiometric Considerations.** Since the “pure” component spectrum of ethylene is so variable, determination of the moles of all observable components is not straightforward. In-



**Figure 4.** Moles of species versus spectrum number for the three primary organometallic species and two organic products. Curve 1: propanal. Curve 2: ketone/polyketone. Curve 3:  $\text{Rh}_4(\text{CO})_{12}$ . Curve 4:  $\text{RCORh}(\text{CO})_4$ . Curve 5:  $\text{RCORh}(\text{CO})_4$ . The 200 data sets correspond to the first 2 days of the first semibatch experiment. The initial conditions were 298.0 mg of  $\text{Rh}_4(\text{CO})_{12}$  and 200 mL of hexane at 20.5 °C, 30 bar ethylene, 4.5 bar CO, 3.5 bar  $\text{H}_2$ . Scale on  $y$ -axis is arbitrary due to widely different concentrations.

deed, even the pure component spectrum of hexane is variable under extreme dilution by ethylene. Instead, we solved a reduced problem where only part of the spectral data was used. The original matrix of spectral data  $A_{366 \times 4751}$  was partitioned. Two spectral windows, 1600–1740 and 2000–2100  $\text{cm}^{-1}$ , were taken and a new composite matrix formed  $A_{366 \times 1202}$ . The hexane absorbance at 1138  $\text{cm}^{-1}$  was used to convert the spectra to a renormalized form,  $A^{\text{pm}}_{366 \times 1202}$ . Information on the moles of rhodium put into the reactor was used as a constraint, and thereby were obtained the moles of the three observable organometallic species  $\text{Rh}_4(\text{CO})_{12}$  and  $\text{RCORh}(\text{CO})_4$  and the moles of rhodium in the new organometallic species  $\text{RCORh}(\text{CO})_3(\pi\text{-C}_2\text{H}_4)$ . Absorptivities from laboratory reference spectra of aldehyde and ketone were used to calculate approximate moles of the organic products. The profiles of moles of species versus spectrum number for the three organometallics and two organics from one of the two sets of data with 200 data points (the 293K semibatch run) are shown in Figure 4. The discontinuous quality of the data arises from the various perturbations in the reaction condition imposed on the system. The primary features to note in Figure 4 are (a) the decline in precursor  $\text{Rh}_4(\text{CO})_{12}$  and associated increase in intermediates  $\text{RCORh}(\text{CO})_4$  and  $\text{RCORh}(\text{CO})_3(\pi\text{-C}_2\text{H}_4)$  and (b) the increases in aldehyde and ketone/polyketone.

The mole data suggest that the approximate maximum ratio of ketone/polyketone to aldehyde in this system was a very significant 0.45. GC–MS was used to confirm the presence of diethyl ketone. Higher molecular weight ketone oligomers could not be identified by the GC–MS analysis.

## Experimental Section

**General Information.** All solution preparations were carried out under argon (99.9995%, Soxal, Singapore) using standard Schlenk techniques.<sup>11</sup> The argon was further purified prior to use by passage through deoxy and zeolite columns. All reactions were carried out under carbon monoxide (99.97%, Soxal, Singapore) and hydrogen (99.999%, Soxal, Singapore) 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 (Newport, MA) 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 *n*-hexane solvent (stated purity >99.6%, Fluka AG) was refluxed over sodium potassium alloy under argon. Ethylene (99.9%, Soxal, Singapore) was used as obtained.

**Equipment.** Two semibatch experiments were conducted in *n*-hexane as solvent in a 1.5 L high-pressure batch reactor system with in situ FTIR capability. Details of the equipment can be found elsewhere.<sup>8d</sup>

GC-MS was run on an HP6890 (HP-1 methyl siloxane capillary column, 100°C) connected to a HP 5973.

**In Situ Spectroscopic Studies.** Two single semibatch experiments were carried out in the following manner. First 150 mL of *n*-hexane was transferred under argon to the autoclave. The total system pressure was raised to 0.4 MPa CO, and the stirrer and high-pressure membrane pump were started. A solution of 298–374 mg of  $\text{Rh}_4(\text{CO})_{12}$  dissolved in 50 mL of *n*-hexane was prepared, transferred to the high-pressure reservoir under argon, pressured with CO, and then added to the autoclave. Ethylene (3.0–4.0 MPa) was then added to the autoclave. Hydrogen (0.5 MPa) was then added to initiate the synthesis. Spectra were recorded every 5 min at 0.2  $\text{cm}^{-1}$  intervals in the range 1000–2500  $\text{cm}^{-1}$ .

In the following steps, the partial pressures of carbon monoxide (0.4–2.4 MPa), hydrogen (0.5–3.0 MPa), and eth-

ylene (3.0–5.0 MPa), the solvent *n*-hexane (200–250 mL), and the reaction temperature (282–293 K) were repeatedly changed. A total of 6 steps were performed in one experiment and 8 steps in another experiment. In each step, ca. 20–40 spectra were taken, and a total of 366 spectra were obtained for the spectroscopic analysis. Mass transfer considerations were taken into account,<sup>12</sup> and in the present configuration, the rate of reaction was very slow compared to transport.

## Computational Section

A newly developed algorithm of band-target entropy minimization (BTEM) was applied for the spectral reconstruction to analyze the spectra. The consolidated experimental spectra were first subjected to a data decomposition approach using singular value decomposition (SVD). The orthogonal basis vectors that spanned the subspace of observations were transformed into pure component spectral estimates using the BTEM algorithm.<sup>10</sup> Details of the mathematical procedures used are described in ref 10.

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