1612 *Organometallics* **2003,** *22,* 1612−1618

Rhodium-Catalyzed Hydroformylation of Alkenes Using in Situ High-Pressure IR and Polymer Matrix Techniques

Jie Zhang, Martyn Poliakoff,* and Michael W. George*

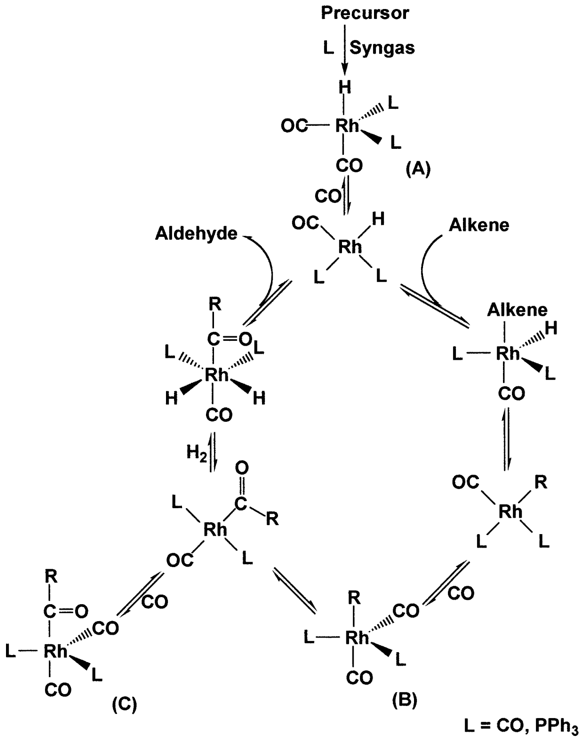
School of Chemistry, University of Nottingham, University Park,
Nottingham, NG7 2RD, United Kingdom

Received October 15, 2002

This paper exploits an unusual high-pressure cell together with in situ FTIR and polymer matrix techniques to study Rh-catalyzed hydroformylation of 1-octene, 1-butene, propene, and ethene, using either Rh(acac)$(CO)_2$ or Rh(acac)(CO)(PPh_3) in a polyethylene matrix. The technique requires only micrograms of catalyst. Using Rh(acac)$(CO)_2$ as the catalyst precursor, we were able to characterize the previously observed acyl rhodium tetracarbonyl intermediates, RC(O)Rh$(CO)_4$, using IR spectroscopy. For the PPh_3-modified reactions, the analogous acyl rhodium tricarbonyl triphenylphosphine intermediates, RC(O)Rh$(CO)_3(PPh_3)$, have been observed. The IR spectra suggest a trigonal-bipyramidal structure with the acyl ligand and the PPh_3 ligand occupying the axial positions. The acyl rhodium tetracarbonyl intermediates, RC(O)Rh$(CO)_4$, can easily react with ethene to form acyl rhodium tricarbonyl ethene species RC(O)Rh$(CO)_3(C_2H_4)$, again identified via IR. The resulting hydroformylation products were extracted from the polyethylene film after the reaction and analyzed by GC. The results indicate that, in the PE matrix, the PPh_3-modified hydroformylation gives a higher linear-to-branched ratio for the unsymmetrical alkenes.

Introduction

Scheme 1. Catalytic Cycle for Rh-Catalyzed Hydroformylation



Rhodium-catalyzed hydroformylation has received a great deal of attention from both academia and industry. Since the early 1960s, this type of reaction has been the subject of numerous mechanistic studies.[1−15] Although the general mechanistic concepts proposed by Wilkinson and co-workers[4] are still accepted as being essentially correct, many of the intermediates involved in the catalytic cycle (see Scheme 1) remain elusive. For unmodified reactions (L = CO), the acyl rhodium intermediates (C) have been observed in more than 20 cases using in situ IR spectroscopic techniques.[12] The observation of the ethyl rhodium intermediate (B) has also been assigned.[14,16] The hydride rhodium intermediate (A) has only very recently been observed under hydroformylation conditions;[17] however its existence had

---

* Corresponding authors. Fax: +44 (0)115 951 3058. E-mail: Martyn.Poliakoff@nottingham.ac.uk; Mike.George@nottingham.ac.uk.

(1) Bath, S. S.; Vaska, L. *J. Am. Chem. Soc.* **1963**, *85*, 3500.

(2) Osborn, J. A.; Wilkinson, G.; Young, J. F. *Chem. Commun. (London)* **1965**, 17.

(3) Vaska, L. *J. Am. Chem. Soc.* **1966**, *88*, 4100.

(4) Evans, D.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3133.

(5) Yagupsky, G.; Brown, C. K.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 1392.

(6) Unruh, J. D.; Christenson, J. R. *J. Mol. Catal.* **1982**, *14*, 19.

(7) Moasser, B.; Gladfelter, W. L.; Roe, D. C. *Organometallics* **1995**, *14*, 3832.

(8) Schmid, R.; Herrmann, W. A.; Frenking, G. *Organometallics* **1997**, *16*, 701.

(9) van Rooy, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Organomet. Chem.* **1997**, *535*, 201.

(10) Matsubara, T.; Koga, N.; Ding, Y.; Musaev, D. G.; Morokuma, K. *Organometallics* **1997**, *16*, 1065.

(11) Feng, J.; Garland, M. *Organometallics* **1999**, *18*, 417.

(12) Liu, G.; Volken, R.; Garland, M. *Organometallics* **1999**, *18*, 3429.

(13) Bianchini, C.; Lee, H. M.; Meli, A.; Vizza, F. *Organometallics* **2000**, *19*, 849.

(14) Liu, G.; Garland, M. *J. Organomet. Chem.* **2000**, *613*, 124.

(15) van der Slot, S. C.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Iggo, J. A.; Heaton, B. T. *Organometallics* **2001**, *20*, 430.

(16) King, R. B.; King, A. D., Jr.; Iqbal, M. Z. *J. Am. Chem. Soc.* **1979**, *101*, 4893.

10.1021/om020854n CCC: $25.00

been demonstrated earlier by employing drastic synthetic conditions using high-pressure IR.[18] For triphenylphosphine-modified reactions (L = PPh_3), the hydride rhodium intermediates (A) have been characterized fully using in situ IR[19] and NMR[20] techniques, and the acyl rhodium intermediates (C) have been observed in in situ NMR experiments.[20−22]

The two most frequently used techniques for mechanistic study of hydroformylation are high-pressure NMR and high-pressure IR spectroscopy. However, both high-pressure NMR and high-pressure IR have shortcomings, and the crucial intermediates may still escape direct observation.[19] In high-pressure NMR experiments,[7,23−27] high concentrations are required in order for the signal-to-noise ratios to be satisfactory. At these high concentrations the reactions usually deviate considerably from catalytic experiments. High-pressure IR techniques[23,28−33] do not suffer from this limitation. However, while reflectance high-pressure IR spectroscopy is a real in situ technique, transmission high-pressure IR spectroscopy has the drawback that the cell must be connected to the autoclave via a suitable delivery system. Transportation from the autoclave to the cell to obtain the spectra can mean that the results are not necessarily representative of the contents of the autoclave. Furthermore, once an autoclave is involved in the experiment, a considerable quantity of catalyst is always required no matter which method is used.

For several decades, matrix isolation has been one of the major techniques for characterizing intermediates in organometallic reactions.[34] Quite recently, we developed a miniature high-pressure low-temperature copper cell[35,36] which allowed us to use polyethylene (PE) matrixes in combination with high-pressure gases. In this way, we have studied intermediates in homogeneously catalyzed hydrogenation.[37,38] Our strategy has been to impregnate a substrate and a catalyst into a PE film and to surround this film by a high pressure of hydrogen. The reaction then takes place inside the PE film, and the various intermediates formed during the reaction can be characterized using IR spectroscopy. The technique requires only micrograms of chemicals and greatly facilitates the investigations of organometallic reactions involving gaseous reactants, for the gaseous reactants can be easily removed from the reaction system, or one type of reactant can be easily replaced by another. The effects of diffusion of gases into and out of the PE film have been studied in some detail.[39] In this paper, our aim has been to validate the use of our cell for studying hydroformylation of alkenes catalyzed by rhodium catalysts. Our strategy has been (i) to use this technique to obtain the spectra of acyl rhodium tetracarbonyl intermediates $RC(O)Rh(CO)_4$ in the unmodified rhodium-catalyzed hydroformylation of 1-octene and compare our results with the published data, (ii) to extend these studies to other alkenes especially gaseous alkenes, (iii) to search for the corresponding acyl rhodium tricarbonyl triphenylphosphine intermediates $RC(O)Rh(CO)_3(PPh_3)$ when the reactions are carried out in the presence of PPh_3, and (iv) to study the rhodium-catalyzed hydroformylation of ethene with and without PPh_3. We have successfully observed not only the well-documented acyl rhodium tetracarbonyl intermediates in the unmodified reactions but also, for the first time, the acyl rhodium tricarbonyl triphenylphosphine intermediates in the triphenylphosphine-modified reactions. We also found that the rhodium carbonyl species at 2089, 2038, and 2017 cm^{-1} formerly observed in the unmodified rhodium-catalyzed hydroformylation of ethene under lower CO pressure and assigned to the ethyl rhodium tetracarbonyl intermediate $C_2H_5Rh(CO)_4$ is in fact an acyl rhodium tricarbonyl ethene species $C_2H_5C(O)Rh(CO)_3(C_2H_4)$. This species is formed by the reaction of acyl rhodium tetracarbonyl intermediates with ethene.

Experimental Section

General Strategy. Dicarbonylacetylacetonato rhodium(I) (99%, Strem), ethene (99%, Air Products), propene (99%, BOC Gases), 1-butene (99%, Aldrich), 1-octene (99%, Aldrich), triphenylphosphine (99%, Acros), and syngas (1/1, Air Products) were used as received. Hostalen GUR 4150 polyethylene (HPE) was supplied by Hoechst.[40] Our previous investigations have shown that this form of PE has a very low degree of unsaturation and have demonstrated that interaction between olefinic double bonds in the PE and unsaturated photofragments is negligible.[41] The PE film was melting pressed at 155 °C from powders using a constant thickness film-maker (Specac P/N 15620). The thickness of the PE film was 0.5 mm. GC analysis was carried out on a Shimadzu GC-17A gas chromatograph with a RTX-5 column.

Preparation of the Catalyst Film. For the unmodified reactions, the catalyst film was made by impregnating Rh(acac)$(CO)_2$ into PE film. The impregnation was achieved by

---

[17] Li, C.; Widjaja, E.; Chew, W.; Garland, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3786.

[18] Vidal, J. L.; Walker, W. E. *Inorg. Chem.* **1981**, *20*, 249.

[19] Dieguez, M.; Claver, C.; Masdeu-Bulto, A. M.; Ruiz, A.; van Leeuwen, P. W. N. M.; Schoemaker, G. C. *Organometallics* **1999**, *18*, 2107.

[20] Brown, J. M.; Kent, A. G. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1597.

[21] Yagupsky, M.; Brown, C. K.; Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 937.

[22] Brown, J. M.; Kent, A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 723.

[23] Moasser, B.; Gladfelter, W. L. *Inorg. Chim. Acta* **1996**, *242*, 125.

[24] Kegl, T.; Kollar, L.; Radics, L. *Inorg. Chim. Acta* **1997**, *265*, 249.

[25] Castellanos-Paez, A.; Castillon, S.; Claver, C.; van Leeuwen, P. W. N. M.; de Lange, W. G. J. *Organometallics* **1998**, *17*, 2543.

[26] Elsevier, C. J. *J. Mol. Catal.* **1994**, *92*, 285.

[27] Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388.

[28] Trzeciak, A. M.; Ziolkowski, J. J. *J. Mol. Catal.* **1986**, *34*, 213.

[29] Moser, W. R.; Papile, C. J.; Brannon, D. A.; Duwell, R. A.; Weininger, S. J. *J. Mol. Catal.* **1987**, *41*, 271.

[30] Garland, M.; Bor, G. *Inorg. Chem.* **1989**, *28*, 410.

[31] Jongsma, T.; Challa, G.; Van Leeuwen, P. W. N. M. *J. Organomet. Chem.* **1991**, *421*, 121.

[32] van Rooy, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Goubitz, K.; Fraanje, J.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 835.

[33] Horvath, I. T. *Organometallics* **1986**, *5*, 2333.

[34] See, for example: Almond, M.; Downs, A. J. *Adv. Spectrosc.* **1989**, *17*.

[35] Cooper, A. I.; Poliakoff, M. *Chem. Phys. Lett.* **1993**, *212*, 611.

[36] Cooper, A. I. Ph.D. Thesis, University of Nottingham, 1994.

[37] Poliakoff, M.; George, M. W. *J. Phys. Org. Chem.* **1998**, *11*, 589.

[38] Childs, G. I.; Cooper, A. I.; Nolan, T. F.; Carrott, M. J.; George, M. W.; Poliakoff, M. *J. Am. Chem. Soc.* **2001**, *123*, 6857.

[39] Goff, S. E. J.; Nolan, T. F.; George, M. W.; Poliakoff, M. *Organometallics* **1998**, *17*, 2730.

[40] HPE is made using a Ziegler−Natta catalyst. It has an extremely high average molecular weight (7.3×10^6), a density of 0.93 g/cm^3, 52% crystallinity, a melting temperature of 130−135 °C, and a remarkable toughness at very low temperatures (Hoechst: Hostalen GUR−Ultrahigh Molecular Weight Polyethylene (PE−UHMW); Hoechst Aktiengesellschaft: Frankfurt, 1993.

[41] Clarke, M. J.; Howdle, S. M.; Jobling, M.; Poliakoff, M. *J. Am. Chem. Soc.* **1994**, *116*, 8621.

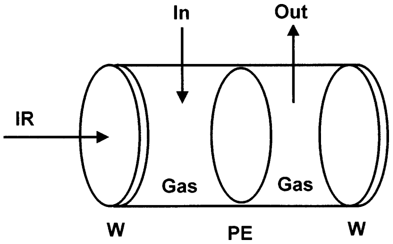


Figure 1. Schematic representation of the high-pressure Cu cell used in the experiments described here. A gas can be introduced to (or removed from) the cell at any time. The gas can freely permeate around the polyethylene catalyst film (PE) where the reactions take place. The reactions are monitored through the CaF_2 windows (W) using in situ FTIR.

placing a PE film in a cyclohexane solvent saturated with dicarbonylacetylacetonato rhodium(I) and leaving it in the solvent for ca. 5 h. For the PPh_3-modified reactions, the catalyst film was made by forming Rh(acac)(CO)(PPh_3) compound in situ inside PE film. The formation of Rh(acac)(CO)(PPh_3) in PE film was achieved by the following steps. First, a PE film was placed in cyclohexane saturated with triphenylphosphine and left for ca. 4 h. In this way, some triphenylphosphine was impregnated into the PE film. Second, the PPh_3-impregnated PE film was transferred to a cyclohexane solvent saturated with dicarbonylacetylacetonato rhodium(I) and left until Rh(acac)$(CO)_2$ in the film is detectable by FTIR. In this way, all the impregnated PPh_3 in the PE film was converted into Rh(acac)(CO)(PPh_3). Finally, the film was placed in clean cyclohexane solvent until all of the free Rh(acac)$(CO)_2$ was extracted. In this way, all excess Rh(acac)$(CO)_2$ was removed, leaving only Rh(acac)(CO)(PPh_3) in the film.

Hydroformylation Experiments. Hydroformylation reactions were carried out in the high-pressure cell, which has been described in detail elsewhere (see Figure 1).[35,37] Briefly, the catalyst PE film was clipped into the cell (for hydroformylation of liquid alkene, the substrate was impregnated into the film in advance together with the catalyst) and the cell was evacuated. An appropriate pressure of syngas ($CO/H_2 = 1/1$) was then added at room temperature (for hydroformylation of gaseous alkenes, a mixture of alkene and syngas was used). The reaction took place inside the PE film at room temperature and was monitored in situ by IR spectroscopy. After the required time, the reaction was quenched by venting the gas mixture, and IR spectroscopy was used to characterize and monitor the decay of the intermediates. Venting and exchanging gases is very rapid, taking less than 1 min for the entire procedure.

Spectroscopy. All IR spectra were recorded on a Nicolet Avatar 360 FTIR interferometer with a liquid nitrogen cooled HgCdTe detector interfaced to a PC running OMNIC software. The resolution was set to 4 cm^{-1} for all measurements. All structure assignments are based on IR spectra.

Results and Discussion

Preparation of the Catalyst Film. Rh(acac)$(CO)_2$ was impregnated into PE film and used directly as an unmodified catalyst. For triphenylphosphine-modified reaction, Rh(acac)(CO)(PPh_3) was used as the catalyst precursor. Figure 2 shows the IR spectra of Rh(acac)$(CO)_2$ and Rh(acac)(CO)(PPh_3) in the PE film. The corresponding peak positions are listed in Table 1. The presence of Rh(acac)(CO)(PPh_3) can be confirmed by comparison with published results.[42]

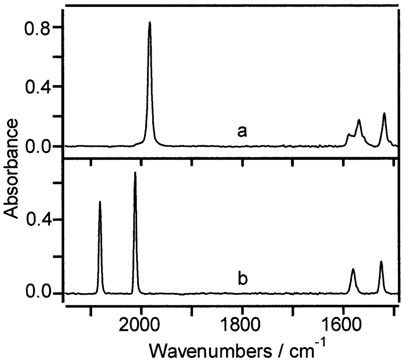


Figure 2. IR spectra of the catalyst precursors in PE film: (a) Rh(acac)(CO)(PPh_3); (b) Rh(acac)$(CO)_2$.

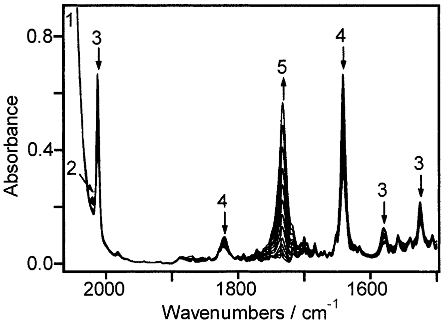


Figure 3. In situ IR spectra of unmodified Rh-catalyzed hydroformylation of 1-octene at 298 K and 1950 psi of syngas ($CO/H_2 = 1/1$) using Rh(acac)$(CO)_2$ as the catalyst precursor. The peaks are labeled as follow: (1) free CO inside the cell; (2) the acyl rhodium tetracarbonyl intermediate $C_8H_{17}C(O)Rh(CO)_4$; (3) Rh(acac)$(CO)_2$; (4) 1-octene; (5) the hydroformylation products $C_8H_{17}CHO$.

Table 1. Peak Positions (cm^{-1}) of the IR Spectra of the Catalyst Precursors

species	ν(CO)	ν(acac)	medium	ref
Rh(acac)(CO)(PPh_3)	1980	1568, 1517	Nujol	42
Rh(acac)(CO)(PPh_3)	1982	1569, 1518	PE	this work
Rh(acac)$(CO)_2$	2081, 2012	1581, 1525	PE	this work

Unmodified Rh-Catalyzed Hydroformylation of 1-Octene, 1-Butene, and Propene in PE Film. The unmodified rhodium-catalyzed hydroformylation of alkenes has been investigated by Garland and co-workers in detail.[11,12,14,30] We investigated this reaction using the Rh(acac)$(CO)_2$-impregnated PE film as catalyst to both validate our approach and to capture any possible new intermediates in the catalytic cycle.

Initially, we used 1-octene as the substrate. Figure 3 shows the in situ IR spectra of this reaction at 298 K under 1950 psi of syngas ($CO/H_2 = 1/1$). The absorptions at 2012, 1581, and 1525 cm^{-1} (labeled 3) are assigned to Rh(acac)$(CO)_2$, and the absorptions at 1821 and 1641 cm^{-1} (labeled 4) are due to 1-octene. The absorption at 1733 cm^{-1} (labeled 5) indicates the formation of the hydroformylation product (nonyl aldehyde). The weak absorption at 2018 cm^{-1} (labeled 2) is attributed to the acyl rhodium tetracarbonyl intermediate.[12] The CO in the syngas surrounding the PE film gives a very broad absorption in the range 2030−2230 cm^{-1} (labeled 1). This band obscures most of the absorptions of interest, but this is not a problem because the intermediates are trapped in the PE film. We can stop the reaction at anytime by venting the syngas and then monitor the

---

[42] Bonati, F.; Wilkinson, G. *J. Chem. Soc.* **1964**, 3156.

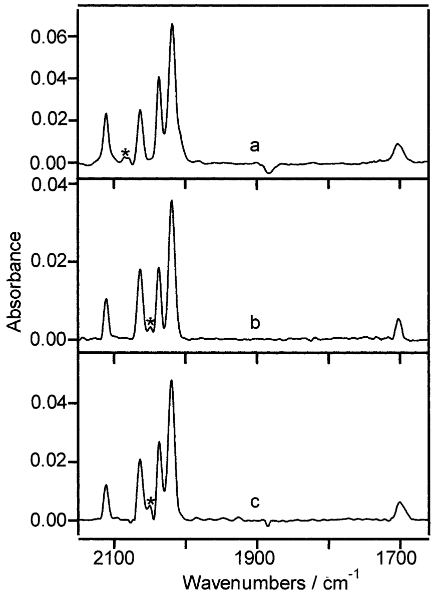


Figure 4. IR spectra derived from the unmodified Rh-catalyzed hydroformylation of (a) 1-octene, (b) 1-butene, and (c) propene at 298 K and 1950 psi of syngas ($CO/H_2 = 1/1$) using $Rh(acac)(CO)_2$ as catalyst precursor. The spectra were obtained by subtractions of the spectra of the PE film taken intermittently after the gas mixture has been removed from the cell. Asterisks (*) indicate bands that have been incompletely removed by subtraction.

Table 2. Peak Positions (cm^{-1}) of the IR Bands of the Intermediates $RC(O)Rh(CO)_4$ Derived from the Unmodified Rh-Catalyzed Hydroformylation of Alkenes

alkene	ν(CO)	ν(C=O)	ref
1-octene	2111, 2064, 2038, 2020	1703	12
1-octene	2110, 2063, 2037, 2018	1703	this work
1-butene	2110, 2063, 2037, 2019	1702	this work
propene	2111, 2064, 2037, 2019	1701	this work
ethene	2111, 2063, 2038, 2019	1696	this work

decay of the intermediates by IR spectroscopy. Subtractions of these spectra give the bands of the intermediates (see Figure 4a). The pattern and the peak positions (see Table 2) of the intermediate spectra are almost identical to the well-documented acyl rhodium tetracarbonyl intermediates $C_8H_{17}C(O)Rh(CO)_4$.[12]

We have extended these studies to the hydroformylation of 1-butene and propene. Subtractions of the spectra of the PE film taken after the syngas had been vented from the cell produced IR spectra that have patterns similar to that of Figure 4a (see Figure 4 and Table 2). Thus, we have successfully obtained the IR spectra of $C_4H_9C(O)Rh(CO)_4$ and $C_3H_7C(O)Rh(CO)_4$, by an approach that is simpler and involves less compound than previous methods.

To confirm that the hydroformylation of alkenes does take place inside the PE film, we carried out solvent extraction (acetone) of the PE film after the reaction and analyzed the extracts by GC. The GC analyses indicate that the hydroformylation reactions were indeed taking place in the PE film and the linear-to-branched ratios obtained from these experiments are very reproducible (see Table 3).

Although we did not detect any new intermediates in these experiments, the results definitely show the effectiveness of our approach for the mechanistic studies of rhodium-catalyzed hydroformylation, especially for the gaseous reactants.

Table 3. Chemoselectivity of the Hydroformylation of Alkenes in PE Film

	linear-to-branched ratio[a]		
catalyst precursor	propene	1-butene	1-octene
$Rh(acac)(CO)_2$	1.0 ± 0.1	1.2 ± 0.1	1.1 ± 0.1
$Rh(acac)(CO)(PPh_3)$	1.7 ± 0.1	3.2 ± 0.1	2.4 ± 0.1

[a] Linear-to-branched ratios are determined by the peak area in the GC spectra.

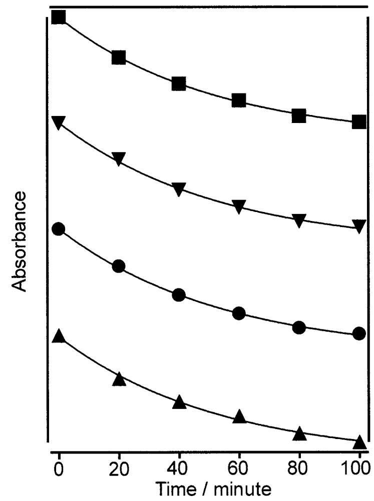


Figure 5. Decay of the four bands at 2055 (▲), 2000 (●), 1981 (▼), and 1681 (■) cm^{-1} in the PPh_3-modified Rh-catalyzed hydroformylation of 1-butene after the syngas has been removed from the cell. Note that the absorbance of the bands has been normalized and offset to emphasize that all four bands decay at the same rate and are therefore due to the same species, $C_4H_9C(O)Rh(CO)_3(PPh_3)$.

PPh_3-Modified Rh-Catalyzed Hydroformylation of 1-Octene, 1-Butene, and Propene in PE Film. Our success in monitoring hydroformylation using the unmodified catalyst prompted us to investigate the PPh_3-modified reactions by making $Rh(acac)(CO)(PPh_3)$ in the PE film (see above). We then used this catalyst film to hydroformylate 1-octene, 1-butene, and propene. In each case, an intermediate was detected with four IR bands at ca. 2056, 2001, 1981, and 1680 cm^{-1}, which disappeared after the syngas was vented from the cell. Figure 5 shows this process for 1-butene. Subtractions of the spectra of PE catalyst film taken sequentially during the decay produced good quality IR spectra (see Figure 6a, b, c). These spectra have patterns very similar to the spectrum of the known cobalt compound $CH_3C(O)Co(CO)_3(PPh_3)$ with the PPh_3 ligand in the apical position.[43] Thus we tentatively attribute these spectra to the acyl rhodium tricarbonyl triphenylphosphine intermediates $RC(O)Rh(CO)_3(PPh_3)$ with equational CO groups (Chart 1). The peak positions are listed in Table 4.

Again, to confirm that hydroformylation was really taking place inside the PE film, we extracted the contents of the PE film after the reaction and analyzed the extracts by GC. As expected, the analysis gave a higher linear-to-branched ratio than with the unmodified reaction (see Table 3).

---

[43] Ford, P. C.; Massick, S. *Coord. Chem. Rev.* **2002**, *226*, 39.

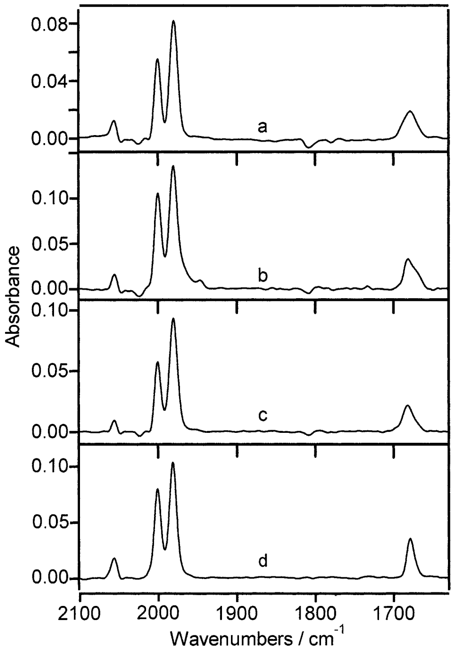


Figure 6. IR spectra derived from the PPh_3-modified Rh-catalyzed hydroformylation of (a) 1-octene, (b) 1-butene, (c) propene, and (d) ethene at 298 K and 1950 psi of syngas ($CO/H_2 = 1/1$) using Rh(acac)(CO)(PPh_3) as catalyst precursor. The spectra were obtained by subtractions of the spectra of the PE film recorded while intermediates decay after the syngas has been removed from the cell.

Chart 1

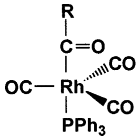


Table 4. Peak Positions (cm^{-1}) of the IR Bands of Intermediates $RC(O)Rh(CO)_3(PPh_3)$ Derived from the PPh_3-Modified Rh-Catalyzed Hydroformylation of Alkenes

alkene	ν(CO)	ν(C=O)
1-octene	2056, 2000, 1980	1681
1-butene	2055, 2000, 1981	1681
propene	2056, 2001, 1981	1681
ethene	2056, 2001, 1981	1679

Very recently, van Leeuwen and co-workers detected the existence of the acyl rhodium diphosphone intermediate $RC(O)RhL_2(CO)_2$ (L = monodentate phosphorus diamide ligand) using in situ IR and NMR techniques.[15] Because several isomers exist for this intermediate, seven absorptions in the terminal CO region were observed in IR spectra. In addition, the strong amide bands of the ligand obscure the expected rhodium-acyl absorption band around 1600–1700 cm^{-1}. In our case, because the precursor has only one PPh_3 ligand in the molecule, it is likely that the acyl rhodium carbonyl intermediates also contain only one PPh_3. The relative intensities of IR bands suggest that the molecule adopts a configuration with the two bulky groups, acyl ligand and triphenylphosphine ligand, occupying the two axial positions with comparatively simple IR spectra in the terminal CO region. The absorption at ca. 1680 cm^{-1} is clearly unsymmetrical in the cases of 1-octene, 1-butene, and propene. This may be due to the two isomers of the acyl ligand (linear and branched). However, as in the case of the acyl rhodium tetracarbonyl intermediate,[12] the isomerization of the acyl ligand appears to have little influence on the IR absorption of other terminally coordinated CO ligands in the acyl rhodium intermediate under the experimental conditions.

Rh-Catalyzed Hydroformylation of Ethene and the Reaction of $RC(O)Rh(CO)_4$ Intermediates with Ethene in PE Film. The unmodified Rh-catalyzed hydroformylation of ethene has also received considerable attention. In 1979, King and co-workers observed infrared absorbance at 2115, 2037, and 2019 cm^{-1} during the hydroformylation of ethene under considerable pressure of CO and attributed these new IR bands to the ethyl rhodium tetracarbonyl intermediate C_2H_5-$Rh(CO)_4$.[16] Very recently, Garland and co-workers reinvestigated this system in more detail.[14] Garland found that this system is difficult to study using IR spectroscopy and complex spectra were obtained. At higher CO partial pressures, the IR spectra correspond exactly to the well-documented mononuclear acyl rhodium tetracarbonyl species (2112, 2068, 2038, and 2020 cm^{-1}). At lower CO partial pressures, bands at 2089, 2038, and 2017 cm^{-1} were obtained. These bands were tentatively attributed to the ethyl rhodium tetracarbonyl intermediate $C_2H_5Rh(CO)_4$. However, it was also noted that these bands could have been due to the acyl species, $C_2H_5C(O)Rh(CO)_3(C_2H_4)$. We have used our technique in an attempt to distinguish between these possibilities.

First, we investigated hydroformylation of ethene using Rh(acac)(CO)(PPh_3) as the catalyst precursor at 298 K under different pressures of syngas and ethene. In every case, we observed the same spectrum, attributed to the acyl rhodium tricarbonyl triphenylphosphine intermediate, $C_2H_5C(O)Rh(CO)_3(PPh_3)$), by comparison with the intermediates in other PPh_3-modified hydroformylation. Unlike the higher olefins, the IR spectrum has a symmetrical absorption around 1680 cm^{-1} (see Figure 6d and Table 4). This is consistent with the fact that there is no possibility of acyl ligand isomerization in the case of $C_2H_5C(O)Rh(CO)_3(PPh_3)$.

We have investigated the unmodified hydroformylation of ethene using $Rh(acac)(CO)_2$ as the catalyst precursor at 298 K under different pressures of syngas and ethene. In these reactions, propionaldehyde was formed (IR and GC), but no ketone or polyketone products were detectable by GC analysis of the extract from the PE film. This contrasts with the recent results[44] from Garland and co-workers where ketone/polyketone were detected in solution reactions involving ethene. With 50 psi of ethene and 1800 psi of syngas ($CO/H_2 = 1/1$), we observed IR bands at ca. 2111, 2088, 2064, 2038, 2017, and 1694 cm^{-1} (Figure 7a), while 700 psi of ethene and 200 psi of syngas ($CO/H_2 = 1/1$) produced IR bands at ca. 2088, 2037, 2015, and 1693 cm^{-1} (Figure 7b). These results are similar to those of Garland in the ν(CO) region.[14] However, in our experiments, these ν(CO) absorptions appear to be associated with an acyl carbonyl absorption. After subtracting spectrum (b) from spectrum (a), bands are found at ca.

---

(44) Li, C.; Guo, L.; Garland, M. The Homogeneous Hydroformylation of Ethylene Catalysed by $Rh_4(CO)_{12}$. The Application of BTEM to Identify a New Rhodium Carbonyl Spectrum. The 13th International Symposium on Homogeneous Catalysis, Tarragona Spain, Sept 3–7, 2002.

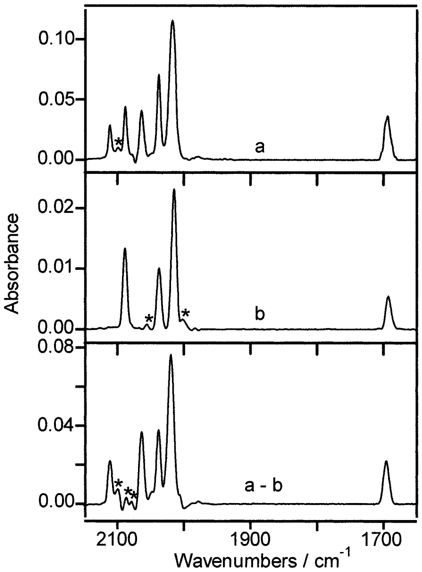
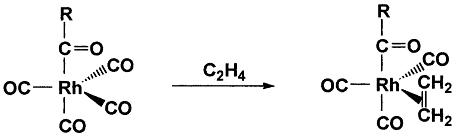


Figure 7. IR spectra derived from the unmodified Rh-catalyzed hydroformylation of ethene using $Rh(acac)(CO)_2$ as the catalyst precursor at 298 K and (a) 50 psi of ethene and 1800 psi of syngas ($CO/H_2 = 1/1$), (b) 700 psi of ethene and 200 psi of syngas ($CO/H_2 = 1/1$). Spectra (a) and (b) were obtained by subtractions of the spectra of the PE film taken after the gas mixture was removed from the cell. Spectra (a − b) were obtained by scaled subtraction of (a) and (b). Asterisks (*) indicate bands that have been incompletely removed by subtraction.

Scheme 2. Interaction of $RC(O)Rh(CO)_4$ with Ethene



2111, 2063, 2038, 2019, and 1696 cm^{-1} (Figure 7(a−b)). By comparison with the higher olefins, these bands can be tentatively assigned to the acyl rhodium tetracarbonyl intermediate $C_2H_5C(O)Rh(CO)_4$. Under higher partial pressure of ethene, $C_2H_5C(O)Rh(CO)_4$ was not observed, but instead there is a second intermediate, spectrum (b). We believe this intermediate to be an acyl rhodium tricarbonyl ethene species, $C_2H_5C(O)Rh(CO)_3(C_2H_4)$, formed by the reaction of $C_2H_5C(O)Rh(CO)_4$ with ethene (Scheme 2). A spectrum very similar to 7b has just been reported by Garland and co-workers.[44]

To support this suggestion, we investigated the reaction of another acyl rhodium tetracarbonyl intermediate, $C_8H_{17}C(O)Rh(CO)_4$, with ethene. Our strategy was to generate $C_8H_{17}C(O)Rh(CO)_4$ by hydroformylation of 1-octene at room temperature (as above), cool the catalyst film to a lower temperature (263 K), and vent the syngas from the cell. The cell was then filled with high-pressure ethene (900 psi), and IR spectroscopy was used to follow the reaction of $C_8H_{17}C(O)Rh(CO)_4$ with ethene over several minutes. Finally, ethene was vented from the cell and IR spectra were used to monitor the decay of the resulting species. Subtraction of these spectra produced an IR spectrum that has peak position and band intensities very similar to those assigned to $C_2H_5C(O)Rh(CO)_3(C_2H_4)$ (see Figure 8b). Spectrum 8b can be reasonably attributed to the acyl rhodium tricarbonyl ethene species $C_8H_{17}C(O)Rh(CO)_3(C_2H_4)$. The absorption at 1996 cm^{-1} is broader and less symmetrical than the corresponding absorption (at 1993 cm^{-1}) in Figure 8a. This is consistent with isomerization of the nonyl ligand (linear and branched). By contrast the $C_2H_5C(O)$ ligand cannot isomerize easily.

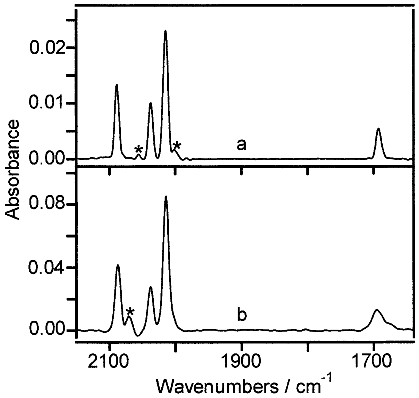


Figure 8. IR spectra from an experiment where an acyl rhodium tetracarbonyl intermediate reacts with ethene: (a) spectrum of the species $C_2H_5C(O)Rh(CO)_3(C_2H_4)$, repeated from Figure 7b; (b) obtained by subtraction of the spectra of the PE film taken after ethene has been removed from the cell containing $C_8H_{17}C(O)Rh(CO)_4$ and ethene at 263 K. Asterisks (*) indicate bands that have been incompletely removed by subtraction. Notice: The patterns of the bands in the two spectra are very similar.

Table 5. Peak Positions (cm^{-1}) of the IR Bands of the Species $RC(O)Rh(CO)_3(C_2H_4)$

species	ν(CO)	ν(C=O)
$C_2H_5C(O)Rh(CO)_3(C_2H_4)$	2088, 2037, 2015	1693
$C_8H_{17}C(O)Rh(CO)_3(C_2H_4)$	2087, 2038, 2014	1696

Our results suggest that the acyl rhodium tetracarbonyl intermediates $RC(O)Rh(CO)_4$ can easily react with ethene to form acyl rhodium tricarbonyl ethene species $RC(O)Rh(CO)_3(C_2H_4)$. We believe that reactions of this type would be difficult if not impossible to carry out in more conventional experiments with spectroscopic autoclaves. The peak positions of the two acyl rhodium tricarbonyl ethene species observed in this work are listed in Table 5.

Conclusions

The rhodium-catalyzed hydroformylation of alkenes has been carried out within a polyethylene film, and the labile acyl rhodium intermediates $RC(O)Rh(CO)_3L$ (L = CO, PPh_3) in the catalytic cycle have been observed. The IR spectra suggest that the intermediates $RC(O)Rh(CO)_3(PPh_3)$ may have a trigonal-bipyramidal structure, with the acyl ligand and the PPh_3 ligand occupying the axial positions, and normally give IR bands at ca. 2056, 2001, 1981, and 1680 (acyl) cm^{-1}. One CO ligand in intermediates $RC(O)Rh(CO)_4$ can be easily replaced by an ethene ligand to form $RC(O)Rh(CO)_3(C_2H_4)$. As expected, the PPh_3-modified Rh-catalyzed hydroformylations in PE film give a higher chemoselectivity for linear aldehyde compared with the unmodified reactions, and the reproducibility is good. We believe that our approach is a valuable addition to the existing techniques for studying such procedures. Although the conditions in our reactions are considerably different from those of industrial hydroformylation reactions, hydroformylation does occur and we can detect and quantify the products from that reaction. It is precisely because of these differences in conditions that we are able to detect species that would be too short-lived or reactive to be observed easily under normal conditions.

Acknowledgment. We thank A. Cowon, Dr. X.-Z. Sun, and Dr. J. Hyde for their collaboration in some experiments, Mr. M. Guyler for his technical support, and the EPSRC for financial support (Grant No. GR/N38312). We thank Professor M. Garland for helpful comments.

OM020854N