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Study of the reaction of $Rh(acac)(CO)_2$ with alkenes in polyethylene films under high-pressure hydrogen and the Rh-catalysed hydrogenation of alkenes

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Abstract

The thermal reaction of $Rh(acac)(CO)_2$ with alkenes has been studied both in the absence and in the presence of high-pressure hydrogen using in situ FTIR and polymer matrix techniques. A series of rhodium alkenes complexes, Rh(acac)(CO)(alkene) (alkene = ethene, propene, 1-butene, 1-octene and *trans*-3-octene), have been characterized using IR spectroscopy. In the presence of a high-pressure hydrogen, catalytic hydrogenation of alkenes was achieved using $Rh(acac)(CO)_2$ within the polyethylene matrix. These results suggest that this hydrogenation process follows the so-called "olefin route" operating via a sequence of ligand loss, binding of an alkene, oxidative addition of hydrogen to the rhodium metal centre, insertion of the coordinated alkene into the M–H bond and finally reductive elimination of the alkane. Rh(acac)(CO) appears to be the active catalytic species in this process. High-pressure polymer matrix techniques have allowed us to unravel some of the interconversions of the catalytic species involved in this catalytic process.

Keywords: Catalytic hydrogenation; Mechanism; Rhodium; Alkene complex; Polymer matrix; In situ FTIR

1. Introduction

There is continuing interest in alkene complexes of transition metals [1–7]. This interest originates partly because these complexes play an important role in understanding the mechanisms of transition metal-catalysed homogeneous reactions involving alkene substrates such as hydrogenation and hydroformylation.

The hydrogenation of alkenes catalysed by mononuclear transition metal catalysts is a well-studied process and there are a wide variety of reaction mechanisms [8–13]. For late transition metal systems, there are several possible mechanistic pathways but five steps are usually involved in the mechanism: (i) ligand loss, (ii) binding of an alkene, (iii) insertion of the alkene into the M–H bond, (iv) oxidative addition of hydrogen to the metal centre and (v) reductive elimination of alkane. However, different catalysts have been shown to follow a different sequence of steps to hydrogenate alkenes [8] (see Scheme 1). Monohydride catalysts, such as $HRh(CO)(PPh_3)_3$, operate via a sequence of (i), (ii), (iii), (iv) and (v) (mechanism A). Cationic catalyst systems, such as $[Rh(S)_2(L)_2]^+X^-$ (S = solvent, L = ligand and $X^- = [PF_6]^-$, $[BF_4]^-$), hydrogenate alkenes via a route of (i), (ii), (iv), (iii) and (v) (mechanism B). Catalysts that form dihydrides such as Wilkinson's catalyst, $RhCl(PPh_3)_3$, often follow a pathway of (i), (iv), (ii), (iii) and (v) (mechanism C). Mechanisms (A) and (B) are known as "olefin" routes while mechanism (C) is known as a hydride route.

The metal hydridoalkyl intermediates (a) in the catalytic cycle may undergo reductive elimination to form the alkane hydrogenation product. This active species may also undergo hydrogen migration to reform the original metal-alkene species and (b) thus provides a pathway by which alkene isomerization can take place. Some catalysts, e.g. $RhCl(PPh_3)_3$, are effective in

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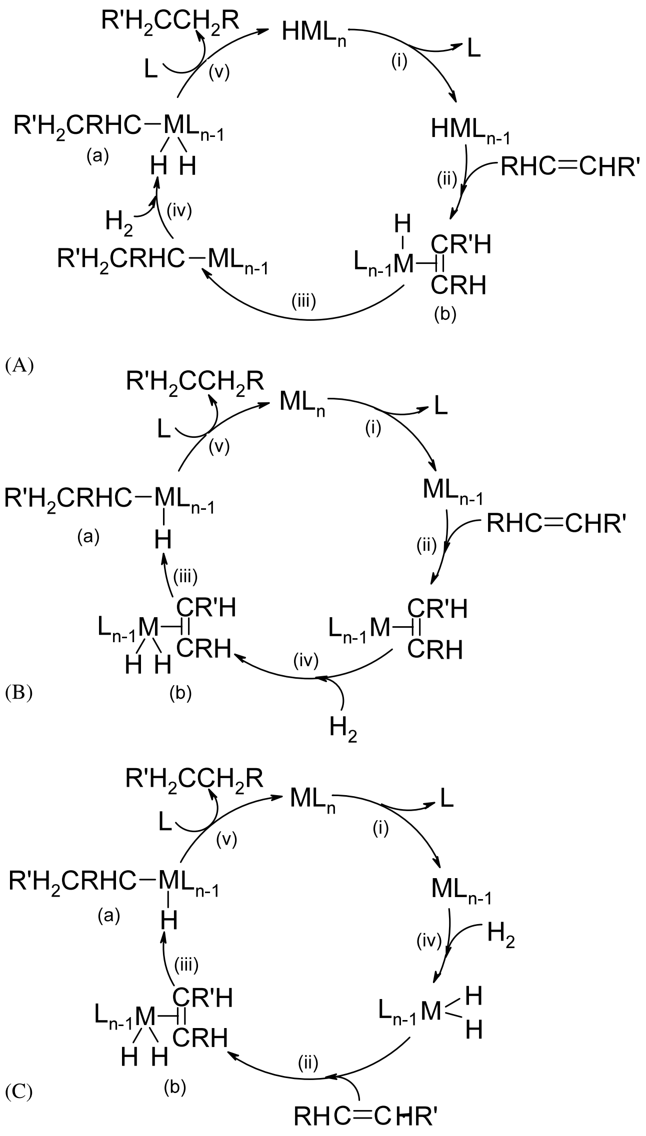


(i) ligand loss; (ii) binding of alkene; (iii) insertion of alkene; (iv) oxidative addition of H_2; (v) reductive elimination of alkane.

Scheme 1.

hydrogenating a wide range of alkenes while others, such as $RhH(CO)(PPh_3)_3$, are specific to certain alkenes, e.g. terminal alkenes are hydrogenated.

It should be noted that many of the conclusions regarding the mechanisms of catalytic hydrogenation have been drawn from kinetic studies. There are far fewer studies [14,15] providing spectroscopic characterization of the intermediates involved in the catalytic cycle. Although rhodium complexes are some of the most widely used catalysts for hydrogenation and $Rh(acac)(CO)_2$ is among the most common, to the best of our knowledge, there have been few reports [16–18] of using $Rh(acac)(CO)_2$ solely as a hydrogenation catalyst.

Polymer matrix isolation combined with in situ high-pressure IR techniques has proved to be effective in studying mechanisms of organometallic reactions [19]. By using this technique, we have successfully carried out mechanistic studies into the photocatalytic hydrogenation of norbornadiene and dimethylfumarate [20,21], and the rhodium-catalysed hydroformylation of alkenes [22]. In this paper, we present an FTIR study of the interaction of $Rh(acac)(CO)_2$ with alkenes in a polyethylene film either in the absence or in the presence of high-pressure hydrogen at 273 K. Our aim has been to trace the active catalytic species in the hydrogenation of alkenes. This technique has allowed us to understand the interconversions of the species involved in the hydrogenation process.

2. Experimental

2.1. General comments

Dicarbonylacetylacetonato-rhodium(I) (99%, Strem), ethene (99%, Air Products), propene (99%, BOC Gases), 1-butene (99%, Aldrich), 1-octene (99%, Aldrich), *trans*-3-octene (98%, Aldrich) and hydrogen (99.99%, Air Products) were used as received. Hostalen GUR 4150 polyethylene (HPE) was supplied by Hoechst [23]. 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 [24]. The PE film was melt-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. 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. Background spectra were recorded with unimpregnated PE film at the experimental temperature. GC analysis was carried out on an SHIMADZU GC-17A gas chromatograph with an RTX-5 column. NMR spectra were recorded on a Bruker AM 300 spectrometer in $CDCl_3$-deuterated solvent.

2.2. IR studies of the interaction of $Rh(acac)(CO)_2$ with alkenes in PE film

The IR studies of the interaction of $Rh(acac)(CO)_2$ with alkenes were carried out in the high-pressure low-temperature cell, which has been described in detail elsewhere [25,26]. For gaseous alkenes, $Rh(acac)(CO)_2$ was impregnated into PE film first. The impregnation was achieved by placing a PE film in a cyclohexane solvent saturated with dicarbonylacetylacetonato rhodium(I) and leaving it to soak for ca. 5 h. The $Rh(acac)(CO)_2$-impregnated PE film was then placed into the cell. The cell was evacuated and an appropriate pressure of alkenes was added. The cell was cooled to the required temperature, and the interaction of Rh(acac)$(CO)_2$ with alkenes was monitored using FTIR spectroscopy. Addition of an appropriate pressure of H_2 allows the hydrogenation of alkenes over Rh(acac)$(CO)_2$ to be monitored in situ. For liquid alkenes, the substrate was impregnated into the PE film in advance together with Rh(acac)$(CO)_2$. The impregnation was achieved by placing a PE film in the corresponding alkene solvent saturated with dicarbonylacetylacetonato rhodium(I) and leaving it for ca. 24 h. The remainder of the procedure was the same as for hydrogenation of gaseous alkenes.

3. Results and discussion

3.1. Reaction of Rh(acac)$(CO)_2$ with alkenes in the absence of hydrogen

At room temperature, alkenes can slowly react thermally with Rh(acac)$(CO)_2$ to form new rhodium carbonyl species. When Rh(acac)$(CO)_2$ is dissolved in liquid alkenes or Rh(acac)$(CO)_2$ interacts with gaseous alkenes in PE film, new IR absorptions in the range 2000–2010 cm^{-1} are always observed. After the bands of Rh(acac)$(CO)_2$ and free alkenes have been subtracted, a three-band IR spectrum is obtained (see Fig. 1). In each case, the new bands can only be observed in the presence of a considerable quantity of alkenes and in the absence of carbon monoxide. Introducing CO into the PE film resulted in a rapid disappearance of these new bands and a corresponding regeneration of the bands of the parent Rh(acac)$(CO)_2$. The new bands are assigned to Rh(acac)(CO)(alkene) formed by alkene substitution one CO ligand in Rh(acac)$(CO)_2$ molecule. The peak positions of the IR bands of these species are listed in Table 1.

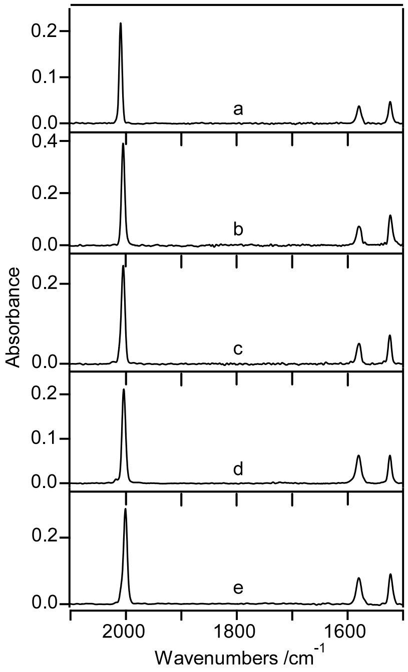


Fig. 1. IR spectra of the Rh(acac)$(CO)_2$/alkenes system in PE film after Rh(acac)$(CO)_2$ and alkenes are subtracted. The alkenes are (a) ethene, (b) propene, (c) 1-butene, (d) 1-octene and (e) *trans*-3-octene.

We have been unable to isolate Rh(acac)(CO)(alkene); nevertheless, an NMR study of Rh(acac)(CO)(1-octene) has been performed. The ^{1}H-NMR spectra showed that the two singlets of Rh(acac)$(CO)_2$ (δ 5.62 (1H, CH) and δ 2.09 (6H, $2CH_3$) ppm) can be distinguished easily from the three singlets of Rh(acac)(CO)(1-octene) (δ 5.45 (1H, CH), δ 2.12 (3H, CH_3 *trans* to 1-octene) and δ 1.92 (3H, CH_3 *cis* to 1-octene) ppm) for the seven protons on the coordinated acac ligand.

Compounds of the type Rh(acac)$(alkene)_2$ are well known and widely studied [27–33]. Surprisingly, only one Rh(acac)(CO)(alkene) compound, Rh(acac)(CO)(cyclooctene), has ever been reported [34,35]. For Rh(acac)$(alkene)_2$, the seven protons on the coordinated acac ligand normally give two singlets at δ 5.00–5.30 (1H, CH) and δ 1.70–1.97 (6H, $2CH_3$) ppm in ^{1}H-NMR spectra [29]. These results are in accordance with the corresponding ^{1}H-NMR data of Rh(acac)(CO)(1-octene) obtained in this work. It was found that Rh(acac)$(alkene)_2$ can readily react with CO to form Rh(acac)$(CO)_2$ irreversibly even in the solid state, and only cyclooctene can replace a single CO ligand in Rh(acac)$(CO)_2$ to form Rh(acac)(CO)(cyclooctene) in solution. However, our experiments indicate that substituting one CO ligand in Rh(acac)$(CO)_2$ by other alkenes is also possible provided that considerable amounts of alkene are present in the reaction system.

3.2. Reaction of Rh(acac)$(CO)_2$ with alkenes in the presence of high-pressure hydrogen

To investigate the hydrogenation process of alkenes over Rh(acac)$(CO)_2$, we introduced high-pressure hydrogen to the Rh(acac)$(CO)_2$/alkenes system. Fig. 2 shows the in situ IR spectra of the Rh(acac)$(CO)_2$/1-octene system in PE film following the addition of high-pressure hydrogen (1400 psi) at 273 K. The bands

Table 1
Peak positions (cm^{-1}) of the IR bands of Rh(acac)(CO)(alkene) in PE film at 273 K

Alkenes	ν(CO)	ν(acac)
Ethene	2010	1580, 1523
Propene	2005	1580, 1523
1-Butene	2005	1579, 1524
1-Octene	2004	1580, 1524
trans-3-Octene	2001	1580, 1523

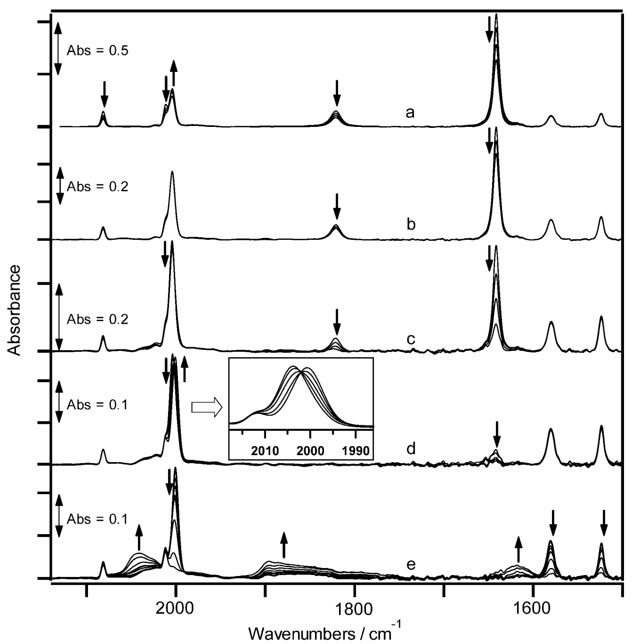


Fig. 2. In situ IR spectra of the Rh(acac)(CO)$_2$/1-octene system in PE film following the addition of high-pressure H_2 (1400 psi) at 273 K. The whole process is divided into five stages (a–e).

corresponding to 1-octene at 1821 and 1641 cm^{-1} decrease showing that 1-octene is consumed. The ν(CO) bands of Rh(acac)(CO)$_2$ at 2081 and 2011 cm^{-1} also decrease, while the bands corresponding to the coordinated acac ligand at ca. 1580 and 1524 cm^{-1} remain unchanged until the end of this process. Fig. 2 shows that there are several overlapping bands around 2000 cm^{-1} region, and there appears to be interconversion between different species.

Our spectra show that the whole process can be divided into five stages. (a) 1-Octene is consumed, and the catalyst precursor Rh(acac)(CO)$_2$ is converted into Rh(acac)(CO)(1-octene). (b) 1-Octene continues to be consumed. However, at this stage there is a little change in Rh(acac)(CO)$_2$ and Rh(acac)(CO)(1-octene) absorptions. (c) 1-Octene continues to be consumed, and Rh(acac)(CO)(1-octene) also starts being consumed slowly. (d) 1-Octene has been consumed completely and Rh(acac)(CO)(1-octene) is converted into a new species with a terminal ν(CO) band at ca. 2001 cm^{-1}. (e) This newly formed species is consumed as indicated by the disappearance of the band at 2001 cm^{-1}, with the concomitant loss of the two bands at 1580 and 1524 cm^{-1} corresponding the coordinated acac ligand. There is formation of three new broad bands at ca. 2042, 1885 and 1620 cm^{-1}, and a blackened PE film indicative of small Rh particles trapped in PE is obtained at the end of this stage.

Venting the high-pressure H_2 from the cell stops the reaction at any time. This allows us to analyse the composition of the reaction mixture within the film at any stage of the catalytic cycle. The contents of the PE film at the end of each stage were extracted with acetone and the extracts were analysed by GC. The results are listed in Table 2. Clearly, hydrogenation and isomerization of 1-octene were taking place in the PE film.

Identical results were obtained using 1-butene as the substrate. However, when ethene or propene was used as the substrate, somewhat different results were obtained. In the case of 1-octene or 1-butene, after the substrate is consumed, the Rh(acac)(CO)(1-octene) or Rh(acac)(CO)(1-butene) species is converted into a new metal carbonyl species with a terminal ν(CO) band at ca. 2001 cm^{-1} (see Fig. 2d). While in the case of ethene or propene, this new metal carbonyl species is not observed after the substrate is completely consumed. Instead, the Rh(acac)(CO)(ethene) or Rh(acac)(CO)(propene) species decompose directly producing the three broad bands at ca. 2042, 1885 and 1620 cm^{-1} as in the case of 1-octene or 1-butene. Fig. 3 shows the in situ IR spectra of the Rh(acac)(CO)$_2$/propene system in PE film following the addition of high-pressure hydrogen (1400 psi) at 273 K.

If the PE film containing Rh(acac)(CO)$_2$ is exposed to high-pressure H_2 in the absence of alkenes, Rh(acac)(CO)$_2$ decomposes directly and the blackened PE film is also obtained. It takes about 10 h for Rh(acac)(CO)$_2$ to decompose completely at room temperature and 1–2 days at 0 °C.

The broad band at ca. 1620 cm^{-1} in Fig. 2e is due to uncoordinated Hacac. This can be confirmed by the FTIR spectra of an authentic 2,4-pentanedione (Hacac) sample in PE film.

If CO is introduced into the reaction system after the substrate alkene has been completely consumed but before the bands due to the coordinated acac ligand begin to decrease, Rh(acac)(CO)$_2$ is quickly reformed as indicated by the regeneration of the band at 2011 cm^{-1}.

It should be noted that the terminal ν(CO) band (2001 cm^{-1}) of the newly formed species in the hydrogenation of 1-octene and 1-butene after the substrate is completely consumed has very similar peak position to that of

Table 2
Analysis of volatile organics extracted from the PE film at the end of different stages of the hydrogenation of 1-octene over Rh(acac)(CO)$_2$ in PE under 1400 psi of H_2 at 273 K (also see Fig. 2)

Stages	Extracts (%)		
	1-Octene	2-Octene	*n*-Octane
Start	100	0	0
1	74.4	8.0	17.6
2	45.5	10.1	44.4
3	26.3	17.5	56.1
4	0	15.4	84.6
5	0	0	100

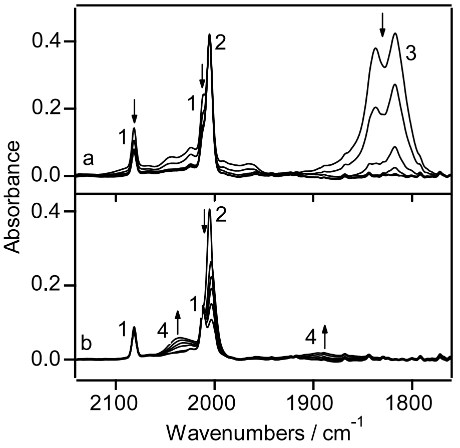
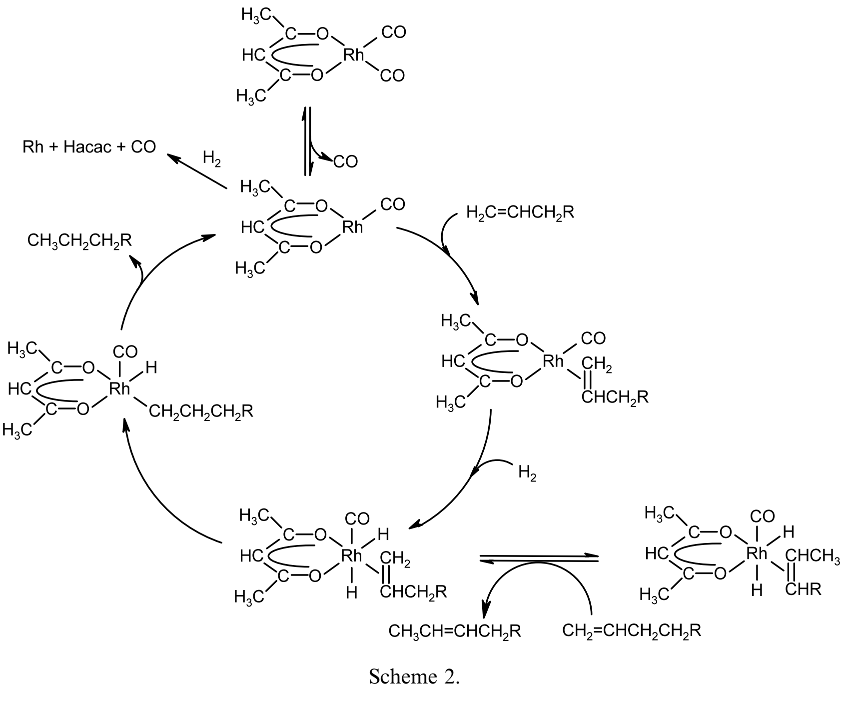


Fig. 3. In situ IR spectra of the Rh(acac)$(CO)_2$/propene system in PE film following the addition of high-pressure H_2 (1400 psi) at 273 K. Spectra (a): propene is being consumed; spectra (b): after propene has been consumed completely. The bands in the spectra are labelled as follow: (1) Rh(acac)$(CO)_2$; (2) Rh(acac)(CO)(propene); (3) absorptions caused by propene itself: the band at higher wavenumbers is caused by free propene gas inside the cell and the band at lower wavenumbers is due to the propene impregnated in the PE film; (4) newly formed bands during the decomposition of Rh(acac)(CO)(propene).

Rh(acac)(CO)(*trans*-3-octene) (see Fig. 2 and Table 1). This band disappears together with the two bands corresponding to the coordinated acac ligand. In addition, this band was not observed in the hydrogenation of ethene and propene, in which no alkene isomerization is involved. From these results, the new species is very probably formed by the reaction of the active Rh(acac)(CO) species with 2-octene or 2-butene, which are formed as by-products through alkene isomerization during the hydrogenation process. 2-Octene or 2-butene can be further hydrogenated to form the same hydrogenation product as that of the original alkenes. Secondary alkenes give very weak or no absorptions in the region of 1500–2100 cm^{-1} in PE film. The secondary alkenes have a poor coordinating ability compared with terminal alkenes because of steric effects. Thus, only after 1-octene or 1-butene has been completely consumed can 2-octene or 2-butene be coordinated to the rhodium centre and finally hydrogenated.

From the above information, we tentatively suggest that the hydrogenation of alkenes over Rh(acac)$(CO)_2$ follows an olefin route in which Rh(acac)(CO) acts as the active catalytic species (see Scheme 2): (i) Rh(acac)$(CO)_2$ undergoes ligand loss first to form the active species Rh(acac)(CO); (ii) an alkene coordinates to rhodium centre of this active species to form Rh(acac)(CO)(alkene); (iii) oxidative addition of hydrogen to the rhodium centre takes place to form the labile intermediate Rh(acac)(CO)(alkene)$(H)_2$; (iv) the coordinated alkene inserts into the M–H bond to form Rh(acac)(CO)(R)(H); (v) reductive elimination of alkane occurs to complete the hydrogenation process and to release the active catalytic species Rh(acac)(CO). Alkene isomerization can also take place during the hydrogenation process to form the alkene isomers. After all alkene in the system is completely consumed, the active Rh(acac)(CO) species decomposes under high-pressure hydrogen to release Hacac and CO. A blackened PE film suggestive of small Rh particles trapped in the PE film is obtained after the reaction. It should be noted that the Rh particles are not responsible for or only contribute very little to the above hydrogenation and isomerization processes because, as indicated by the



Scheme 2.

GC analysis, these processes take place in the PE film before the formation of the Rh metal particles. When CO is introduced after alkenes are consumed, Rh(acac)(CO) will quickly pick up a CO ligand to reform the original Rh(acac)$(CO)_2$. We are not very clear about the origin of the two broad bands at ca. 2042 and 1885 cm^{-1} formed during the decomposition of Rh(acac)(CO). They may be related to a Rh dimer or cluster, which are likely to have bridging CO groups.

4. Conclusion

FTIR studies of the reaction between Rh(acac)$(CO)_2$ and alkenes in PE film have been carried out either in the absence or in the presence of high-pressure hydrogen. Alkenes can substitute one CO ligand in Rh(acac)$(CO)_2$ to form a series of Rh(acac)(CO)(alkene) compounds in the absence of CO and in the presence of considerable quantity of alkenes. Following the so-called “olefin route”, Rh(acac)$(CO)_2$ can catalyse the hydrogenation of alkenes through the active species of Rh(acac)(CO). A complete picture of the interconversions of some catalytic species involved in a catalytic process has been provided for the first time.

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