DALTON

The carbonylation of allylic halides and prop-2-en-1-ol catalysed by triethylphosphine complexes of rhodium†

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In ethanol, $[RhX(CO)(PEt_3)_2]$ added directly or formed *in situ* from $[Rh_2(OAc)_4]\cdot 2MeOH$ (OAc = O_2CMe) and PEt_3 or $[Rh(OAc)(CO)(PEt_3)_2]$ catalysed the carbonylation of $CH_2{=}CHCH_2X$ (X = Cl, Br or I) to ethyl but-3-enoate with $CH_2{=}CHCH_2OEt$ as a side product. Small amounts of the isomerisation product, ethyl but-2-enoate were produced but no base was required for the reaction. The selectivity of the reaction is in the order Cl > Br > I and prop-2-en-1-ol can be successfully carbonylated to prop-2-enyl but-3-enoate by the same system using 3-chloroprop-1-ene as a promoter. 3-Fluoropropene was not carbonylated, but in the presence of H_2 underwent hydroformylation to produce acetals. 3-Chlorobut-1-ene and 1-chlorobut-2-ene both produced ethyl pent-3-enoate and 3-ethoxybut-1-ene. *In situ* and *ex situ* NMR and IR spectroscopic studies have been used to show that the first step of the reaction is oxidative addition to give $[Rh(CH_2CH{=}CH_2)Cl_2(CO)(PEt_3)_2]$ for which thermodynamic parameters have been obtained. Both 3-chlorobut-1-ene and 1-chlorobut-2-ene give $[Rh(CH_2CH{=}CHMe)Cl_2(CO)(PEt_3)_2]$ but with different *E* : *Z* ratios. The detailed mechanism of the oxidative addition is discussed. The CO inserts into the Rh–C bond to give $[Rh(COCH_2CH{=}CH_2)Cl_2(CO)(PEt_3)_2]$, from which but-3-enoyl chloride reductively eliminates to react with ethanol to give the observed products. High-pressure IR and high-pressure NMR studies reveal that $[RhX(CO)(PEt_3)_2]$ (X = Cl or Br) reacts with CO to give $[RhX(CO)_2(PEt_3)_2]$, which exists as two isomeric forms. The compound $[Rh(OAc)(CO)(PEt_3)_2]$ catalyses the formation of prop-2-enyl ethanoate from 1-chloroprop-2-ene and sodium ethanoate. A mechanism is proposed.

The catalytic carbonylation of methanol to give ethanoic acid is one of the most successful examples of the application of homogeneous catalysis to a large-scale industrial process.[1] The key catalytic step is the carbonylation of iodomethane to ethanoyl iodide[2,3] but, despite this, the carbonylation of other organic halides has been much less investigated. During the course of studies on the direct formation of alcohols from hydrocarbonylation of alkenes under mild conditions,[4–7] we sought to extend the scope of the reaction to the use of functionalised substrates. This was successful for, *e.g.* prop-2-en-1-ol,[5] but when using l-chloroprop-2-ene as substrate and ethanol as solvent, a totally different reactivity was observed in that the double bond remained unreacted but Reppe-type chemistry was observed and a major product was the unsaturated ester. Carbonylation of propenyl halides to homologous esters has been observed before using Co,[8] Ni,[9–11] Pd,[12,13] Fe[14] or Rh[15] catalysts, but in general propenyl chlorides show low reactivity, a strong base is required to remove HX (X = Cl, Br or I)[8–14] generated in the reaction and isomerisation of the double bond[9–11,13] or apparent skeletal rearrangement (to esters of 2-methylpropanoic acid)[12] can be competitive side reactions leading to low reaction selectivity.

In this paper, we report detailed studies of the carbonylation of l-halogenoprop-2-enes, the extension to substituted substrates and to the successful chloride-promoted carbonylation of prop-2-en-1-ol. A preliminary communication covering some of this work has appeared[16] and we have reported that the same catalyst system is active for the carbonylation of methanol[17] or the dicarbonylation of diiodomethane to malonate esters.[18,19]

Experimental

The NMR spectra were recorded on a Brüker AM300 spectrometer operating in the Fourier-transform mode with, for ^{13}C and ^{31}P, broad-band ^{1}H decoupling. Chemical shifts are in ppm to high frequency of $SiMe_4$ (^{1}H, ^{13}C) or external 85% H_3PO_4 (^{31}P). Infrared spectra were recorded on a Perkin-Elmer 1720 Fourier-transform spectrometer. Gas chromatographic analyses were carried out on a Phillips PU4500 gas chromatograph using Chromopak software, a 25 m SGE BP-1 (non-polar column) was employed and all samples were quantified against toluene as an internal standard (50 μl cm^{-1}); gas chromatography–mass spectrometry (GCMS) studies were carried out using a Hewlett Packard 5890 GC fitted with a 25 m SGE BP-1 column and interfaced with an INCOS 50 electric quadrupole mass spectrometer.

All manipulations were carried out under dry deoxygenated argon using standard Schlenk-line and catheter-tubing techniques. All solvents were dried by distillation from sodium diphenylketyl [toluene, tetrahydrofuran (thf) or diethyl ether]; sodium (light petroleum, boiling range 40–60 °C); calcium hydride (CH_2Cl_2) or magnesium ethoxide prepared *in situ* from magnesium turnings (ethanol). All reagents were standard laboratory reagents and were used without further purification, unless otherwise stated.

The compound $RhCl_3\cdot 3H_2O$ (Johnson Matthey) was used as received. The compounds $[RhCl(CO)(PEt_3)_2]$,[20] $[RhBr(CO)(PEt_3)_2]$,[21] $[Rh_2(OAc)_4]\cdot 2MeOH$ (OAc = O_2CMe)[22] and $[Rh(OAc)(CO)(PEt_3)_2]$[23] were prepared by standard literature methods.

1-Fluoroprop-2-ene

This compound was prepared by an adaptation of a literature method.[24] 1-Bromoprop-2-ene (12.1 g, 8.65 cm^3, 0.1 mol) was dissolved in diethylene glycol (40 cm^3). Potassium fluoride (11.62 g, 0.2 mol) was added and the solution stirred whilst heating at 120 °C under reflux. The top of the condenser was connected to two Schlenk tubes in series *via* a length of hose which in turn was connected to a drying column. The Schlenk tubes were immersed in a CO_2–acetone bath at −78 °C and the 1-fluoroprop-2-ene (b.p. −3 °C) collected in them as it was formed. Yield: 92% based on 1-bromoprop-2-ene.

† In honour of Sir Geoffrey Wilkinson, FRS, a great friend and mentor as well as a superb chemist.

Preparation of authentic esters and ethers for comparison with reaction products

Esters. Ethyl but-3-enoate and ethyl pent-3-enoate were prepared by dissolving but-3-enoic acid or pent-3-enoic acid (5 cm^3) in ethanol (10 cm^3) and adding 2 drops of concentrated sulfuric acid. After stirring overnight, the solutions were fractionally distilled using an Ace microscale spinning band column. The ester fractions were shown to be pure by GC analysis.

Ethers. Ethyl but-2-enyl ether and 2-ethoxyprop-1-ene were prepared by the Williamson ether synthesis.[25] Sodium (3 g, 0.13 mol) was added to dry ethanol (30 cm^3) in small pieces. Once the formation of sodium ethoxide was complete, 1-chlorobut-2-ene or 3-chlorobut-1-ene (11.77 g, 0.13 mol) was added dropwise whilst the solution was vigorously stirred. After the addition was complete, the solution was heated on a water bath for 1 h and cooled to room temperature. The volatiles were trap-to-trap distilled *in vacuo*. The resulting solutions were then fractionally distilled using a 10 cm Vigreux column. The resulting ethers, ethyl but-2-enyl ether and 2-ethoxyprop-1-ene were shown to be pure by GC analysis.

Reaction of $[RhX(CO)(PEt_3)_2]$ (X = Cl, Br or I) with 3-halogenoprop-1-enes

The compound $[RhX(CO)(PEt_3)_2]$ (0.4 mmol) was dissolved in CD_2Cl_2 (0.5 cm^3). 3-Halogenoprop-1-ene (2.5×10^{-3} mol) was added and the solution cooled to −30 °C. The reactions were monitored by ^{31}P and ^1H NMR spectroscopy. Once complete conversion to the supposed oxidative addition product had occurred, the NMR tube was cooled to −78 °C and its contents transferred to a pre-cooled Schlenk tube. The solutions were allowed to crystallise at −30 °C and the highly thermally sensitive solids obtained were collected and characterised by ^1H and ^{31}P NMR as well as IR spectroscopy. Attempts to crystallise the solids from light petroleum or CH_2Cl_2–light petroleum led to oils.

In situ NMR spectroscopic experiments and measurement of thermodynamic parameters

The compound $[RhCl(CO)(PEt_3)_2]$ (0.09 g 0.23 mmol) was dissolved in CD_2Cl_2 (0.7 cm^3) and the solution cooled to −40 °C. 3-Chloroprop-1-ene (0.0145 g, 0.19 mmol) was added and the NMR tube was transferred to a pre-cooled NMR machine. The ^{31}P and ^1H NMR spectra were measured immediately and after 1 h. (There was no difference between these spectra.) The tube was allowed to warm and spectra were recorded at various temperatures to room temperature. In some cases, the mixing was carried out at room temperature and measurements were made at a variety of temperatures down to −60 °C. Thermodynamic parameters were calculated from integration of ^{31}P NMR spectroscopic resonances (unless otherwise stated). It was assumed that the receptivities of the P atoms in each of the complexes, all of which contain two mutually *trans* PEt_3 units, were the same.

Thermodynamic parameters for the oxidative addition of 1-chlorobut-2-ene (0.036 g, 0.4 mmol) and of 3-chlorobut-1-ene (0.036 g, 0.4 mmol) to $[RhCl(CO)(PEt_3)_2]$ (0.12 g, 0.3 mmol and 0.14 g, 0.35 mmol respectively) in CD_2Cl_2 (0.7 cm^3) were obtained in a similar fashion.

A similar reaction of 1-bromobut-2-ene (0.03 g, 0.25 mmol) with $[RhCl(CO)(PEt_3)_2]$ (0.13 g, 0.325 mmol) in CD_2Cl_2 (0.5 cm^3) was carried out in the high pressure NMR cell and monitored by ^1H and ^{31}P NMR spectroscopy at a variety of temperatures below room temperature. The NMR cell was then pressurised with CO and monitored by ^1H and ^{31}P NMR spectroscopy as the temperature was raised to 100 °C.

Attempted isolation of $[Rh(COCH_2CH{=}CH_2)Cl_2(CO)(PEt_3)_2]$

The compound $[RhCl(CO)(PEt_3)_2]$ (0.5 g, 1.2 mmol) was dried *in vacuo* at 150 °C, cooled and dissolved in 1-chloroprop-2-ene (3 cm^3, 2.9 g, 37 mmol) in a flame-dried glass pressure vessel. The bottle was pressurised with CO (4 bar), closed and heated to 100 °C for 4 h. A dark orange oil separated. After cooling, excess 1-chloroprop-2-ene was decanted and the remaining orange oil dried *in vacuo* for 15 min at 20 °C. Yield 0.5 g, 82%. All attempts to crystallise the oil from a variety of solvents and at temperatures as low as −100 °C were unsuccessful. It was characterised spectroscopically as $[Rh(COCHCH_2{=}CH)Cl_2(CO)(PEt_3)_2]$.

Catalytic production of prop-2-enyl ethanoate from 1-chloroprop-2-ene and sodium ethanoate

1-Chloroprop-2-ene (1 cm^3, 0.012 mol), NaOAc (1.66 g, 0.012 mol) and $[Rh(OAc)(CO)(PEt_3)_2]$ (0.025 g, 6×10^{-5} mol) were dissolved in deoxygenated ethanol (4 cm^3) and heated in a glass pressure vessel at 120 °C for 4 h. The resulting solution was cooled, filtered to remove NaCl and analysed by GLC. No 1-chloroprop-2-ene remained but the major products were prop-2-enyl ethanoate and ethyl prop-2-enyl ether in approximately equal amounts. In the absence of catalyst, only very small amounts of products were obtained and most of the 1-chloroprop-2-ene remained at the end of the reaction.

Autoclave reactions

The steel autoclaves (internal volume 250 cm^3) were fitted with a glass liner containing a magnetic follower specially designed to aid gas mixing. A narrow stem glass funnel was placed in the top of the liner (this prevented distillation of portions of the reaction mixture into the space between the liner and the steel walls and reduced corrosion of the autoclave, but allowed liquid phase reagents to be injected directly into the glass liner). The autoclave was deoxygenated by evacuation and introducing argon (1 bar) three times. With a slow stream of argon passing through the autoclave, the reaction solution [0.05–0.1 mmol of catalyst and substrate (1 cm^3) in deoxygenated ethanol (4 cm^3)] was injected into the liner. The autoclave was pressurised slowly (≈3 bar min^{-1}) to the reaction pressure (usually 40 bar), closed, heated using heating bands to the required temperature, usually 120 °C, at a rate of 20 °C min^{-1} and stirred for the desired reaction time. The autoclave was then cooled in a water bath for 1 h and slowly vented in a fume cupboard. The solutions were analysed by GC or GCMS. In some cases, the solutions were fractionally distilled and the products isolated for spectroscopic characterisation. For reactions involving 1-fluoroprop-2-ene, the autoclave, Schlenk tubes, syringes, *etc.* were all pre-cooled to −20 °C.

Catalytic preparation and purification of ethyl but-3-enoate

The compound $[RhCl(CO)(PEt_3)_2]$ (0.090 g, 0.00022 mol) was dissolved in dried and deoxygenated ethanol (12 cm^3) in a Schlenk tube. 1-Chloroprop-2-ene (2.81 g, 3 cm^3, 0.037 mol) was added to the catalyst solution and stirred. The resulting pale yellow solution was added to a dried and deoxygenated autoclave fitted with a glass liner and magnetic stirrer *via* the anaerobic injection port under a steady stream of argon. The autoclave was sealed and pressurised with carbon monoxide (40 bar) at ambient temperature before being fitted with a heating band and heated to 120 °C at 20 °C min^{-1} and left to react for 4 h. After this time it was cooled to ambient temperature in a water bath and carefully vented in a fume-hood. After venting, the liquid contents of the autoclave were removed *in vacuo* to a liquid nitrogen trap in order to separate them from the catalyst. The resulting colourless solution was distilled using an Ace spinning-band microdistillation apparatus to yield ethyl but-3-enoate as the final fraction. Yield: 1.18 g (28% based on 1-chloroprop-2-ene).

High-pressure NMR spectroscopic studies

A 5 mm sapphire NMR tube was sealed with Araldite adhesive to a pressure head specially designed to sit within an NMR tube

Table 1 Products from carbonylation of organic halides catalysed by rhodium triethylphosphine complexes

Substrate	Catalyst precursor[a]	Conversion/%	Products/%[b]			
			CH_2=$CHCH_2CO_2Et$	CH_3CH=$CHCO_2Et$	CH_2=$CHCH_2OEt$	Dimer[c]
CH_2=$CHCH_2Cl$	A	64	37	12	2.7	*d*
CH_2=$CHCH_2Cl$	—	*e*	0	0	2	*d*
CH_2=$CHCH_2Cl$	B	64	33	*e*	7	*d*
CH_2=$CHCH_2Br$	A	51	25	8	4.8	*d*
CH_2=$CHCH_2Br$	B	91	55	*e*	27	*d*
CH_2=$CHCH_2I$[f]	A	92	20	6	33	*d*
CH_2=$CHCH_2I$	B	88	19	*e*	11	*d*
$MeCH$=$CHCH_2Cl$	C	100	47[g]	8[h]	17[i]	10
$MeCH$=$CHCH_2Cl$	—	*e*	0	0	2[i]	11
CH_2=$CHCH(Me)Cl$	C	100	61[g]	9[h]	16[i]	14
CH_2=$CHCH(Me)Cl$	—	*e*	0	0	7[i]	16
$MeCH$=$CHCH_2Br$	C	100	31[g]	8[h]	22[i]	19
$MeCH$=$CHCH_2Br$	—	*e*	0	0	5[i]	19
CH_2=$C(Me)CH_2Br$	C	10	4[j]	0	<2[k]	*d*
$C_6H_5CH_2Cl$	B	43	2[l]	*e*	41[m]	0
$CH_3CH_2CH_2Cl$	B	0	0	0	0	0
CH_3CH_2I	B	11	0	0	16[n]	0
$(CH_3)_3CBr$[o]	B	15	0	0	13[p]	0
C_6H_5Cl	B	0	0	0	0	0
CH_2=$CHCH_2F$[q]	C	0	0	0	0	0
$ClCH_2CH$=$CHCH_2Cl$	C	90	61[g,r]	0	0	0
CH_2=$CHCH_2OH$	A[s]	96	78[t]	0	4	*d*

[a] A: $[RhCl(CO)(PEt_3)_2]$ (1×10^{-4} mol), RX (1 cm^3), EtOH (4 cm^3), p_{CO} = 40 bar, 120 °C, 4 h; B: $[Rh_2(OAc)_4]\cdot 2MeOH$ (2×10^{-5} mol), PEt_3 (4×10^{-4} mol), RX (1 cm^3), EtOH (4 cm^3), p_{CO} = 40 bar, 120 °C, 4 h; C: $[Rh(OAc)(CO)(PEt_3)_2]$ (1×10^{-4} mol), RX (1 cm^3), EtOH (4 cm^3), p_{CO} = 40 bar, 120 °C, 4 h. [b] Propene and EtX are obtained in all successful reactions. [c] Hexa-1,5-diene for CH_2=$CHCH_2X$; mixture of octa-1,7-diene, 3-methylhepta-1,6-diene and 3,4-dimethylhexa-1,5-diene for CH_2=$CHCH(Me)Cl$ or CH_3CH=$CHCH_2X$. [d] Not quantified but significant amounts detected and identified by GCMS. [e] Not quantified. [f] EtI (91%). [g] *E*-CH_3CH=$CHCH_2COOEt$. [h] *Z*-CH_3CH=$CHCH_2CO_2Et$. [i] CH_2=$CHCH(Me)OEt$ with <3% $MeCH$=$CHCH_2$-OEt. [j] CH_2=$C(Me)CH_2COOEt$. [k] CH_2=$C(Me)CH_2OEt$. [l] $C_6H_5CH_2COOEt$. [m] $C_6H_5CH_2OEt$. [n] Et_2O. [o] 2-Methylpropene detected. [p] $(CH_3)_3COEt$. [q] Using catalyst system A and CO–H_2 (1:1, 40 bar), 1,1-diethoxybutane, 1,1-diethoxy-2-methylpropane and 1,1-diethoxy-4-fluorobutane were produced. [r] CH_3CH=$CHCH_2COOH$ (17%) is also produced. [s] Ethanol was replaced with CH_2=$CHCH_2OH$, RX = CH_2=$CHCH_2Cl$. [t] Assuming 2 mol of CH_2=$CHCH_2OH$ per mol of product (CH_2=$CHCH_2CO_2CH_2CH$=CH_2); CH_2=$CHCH_2CO_2H$ (3%) was also produced.

spinner. The screw-on cap was removed and the apparatus deoxygenated by evacuation and introducing argon (1 bar) three times within a specially designed Schlenk tube. The reaction solution containing catalyst (0.4–0.5 mmol), the substrate and the NMR solvent (0.4 cm^3) was transferred into the NMR tube and the cap replaced. The spinner was removed and the cell transferred into a specially designed steel casing for pressurisation with CO. After pressurisation, the cell was closed, the spinner replaced and the tube was lowered into the NMR machine. All of these procedures were carried out in such a way that the tube was always surrounded by a steel or brass casing until it entered the NMR machine, in order to protect the operator in the event of fracture or explosion.

High-pressure IR studies

A commercial Cylindrical Internal Reflectance (CIR) cell, consisting of a stirrable Parr autoclave, manufactured from Hastelloy C to avoid etching of stainless steel, modified to take the CIR rod, was used for all the high-pressure IR studies. Most reactions were carried out using a single silicon crystal rod since initial studies using ZnSe showed that it was easily etched by the reaction solutions, causing a dramatic reduction in the intensity of the transmitted radiation. The catalyst (*ca.* 1 mmol) was dissolved in the reaction solvent (8 cm^3) containing the substrate (2 cm^3) in a Schlenk tube. The high-pressure IR cell was deoxygenated by passing argon for 15 min before the reaction solution was injected into the cell. The cell was sealed and pressurised to the appropriate temperature at a rate of 2 bar min^{-1}. Heating rods were inserted into holes in the autoclave body and the cell was mounted within a focusing mirror stage directly in the path of the IR beam. A thermocouple was incorporated into a port in the cell and the cell heated to the required temperature. Spectra were recorded at appropriate temperatures and/or after specific reaction times. At the end of the reaction, the cell was allowed to cool in air to room temperature, before being slowly vented in a fume cupboard. The products were sometimes analysed by NMR, GC and/or GCMS.

Results

Catalytic reactions

In the presence of $[Rh_2(OAc)_4]$–PEt_3, $[Rh(OAc)(CO)(PEt_3)_2]$ or $[RhCl(CO)(PEt_3)_2]$, 1-halogenoprop-2-enes can be carbonylated at ≈120 °C and 40 bar in ethanol (see Table 1). The major product obtained is ethyl but-3-enoate but smaller amounts of the isomerised product, ethyl but-2-enoate, ethyl prop-2-enyl ether and C_6 dienes are also produced. No base is added to the reaction mixture so the HX produced reacts with the solvent to give EtX. Small amounts of prop-2-ene are also produced. In the absence of catalyst, no carbonylation products are observed but the C_6 dienes are products and small amounts of the ether are obtained.

The results in Table 1 show that the selectivity to ester over ether products decreases in the order Cl > Br > I (in the substrate) and reflects the ease with which the ether is formed. 3-Fluoroprop-1-ene was not carbonylated in this system, presumably because of the strength of the C–F bond, but in the presence of H_2 acetals of butanal, 2-methylpropanal and 4-fluorobutanal were formed.

Examination of a variety of other substrates indicates that (apart from CH_3I[17] and CH_2I_2,[18,19] which will be reported separately), carbonylation activity is only observed for 1-halogenoprop-2-enes and weakly for benzyl chloride. Alkyl and phenyl halides are unreactive. The product evolution of the carbonylation of 1-chloroprop-2-ene as a function of time is shown in Fig. 1. It is interesting to note that the yield of ether product decreases slightly with time at longer reaction times.

Using either of the methyl substituted substrates, 1-chlorobut-2-ene or 3-chlorobut-1-ene, the products obtained are ethyl *Z*- and *E*-pent-3-enoate and 3-ethoxybut-1-ene (Table 1, Scheme 1) together with C_8 dienes. By contrast, reactions of 1-chlorobut-2-ene or 3-chlorobut-1-ene with NaOEt produce the expected ethyl prop-2-enyl ether and 3-ethoxybut-1-ene respectively. In the absence of catalyst, the carbonylation products are not formed but the C_8 dimers are obtained with the same overall yield. Both straight and branched chain ether products are produced from both substrates. 3-Chloro-2-methylprop-1-ene is hardly carbonylated at all by the same catalyst system.

In an attempt to prepare diesters, which are of importance in polyester manufacture, 1,4-dichlorobut-2-ene was carbonylated using the same system. The products were not the expected diethyl hex-3-en-l,6-dioate and 1,4-diethoxybut-2-ene but rather the main product was ethyl pent-3-enoate together with a trace of pent-3-enoic acid.

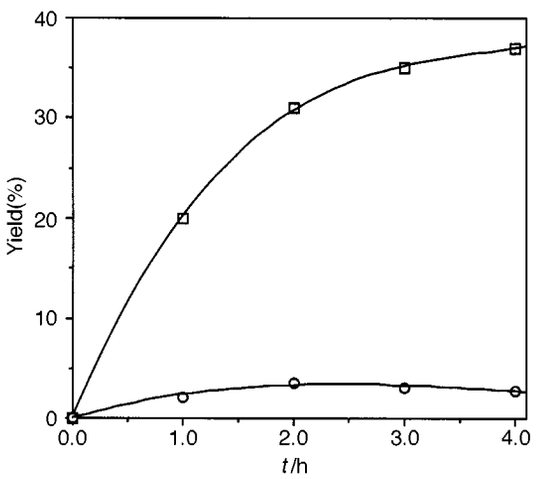
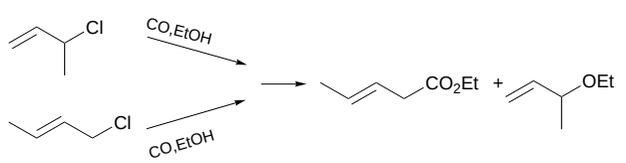


Fig. 1 Product evolution for the carbonylation of 1-chloroprop-2-ene in ethanol catalysed by [RhCl(CO)(PEt_3)$_2$]; (□) ethyl but-3-enoate and (○) ethyl prop-2-enyl ether



Scheme 1 Products from the carbonylation of 1-chlorobut-2-ene and 3-chlorobut-1-ene in ethanol catalysed by [RhCl(CO)(PEt_3)$_2$]

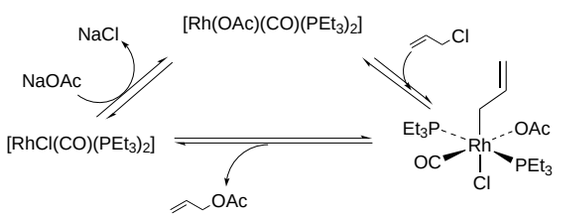
Most of the reactions described above were carried out in ethanol, thus leading to the formation of EtX as a product. It thus appeared that replacing ethanol with prop-2-en-1-ol might give an active system for the catalytic carbonylation of the alcohol. Indeed, the reaction proceeds with high selectivity to produce prop-2-enyl but-3-enoate, with only very small amounts of side products (Table 2). This is an unusual example of an alcohol carbonylation in which chloride is active as a promoter. Iodide is normally preferred or essential.[1]

Finally, during the course of studies of the individual steps of the reaction (see below) we noticed that [Rh(OAc)(CO)(PEt_3)$_2$] reacts with 3-chloroprop-1-ene to give [RhCl(CO)(PEt_3)$_2$] and prop-2-enyl ethanoate. This suggested that this reaction might be carried out catalytically using NaOAc in the presence of [Rh(OAc)(CO)(PEt_3)$_2$]. Indeed, this turns out to be the case with complete conversion to prop-2-enyl ethanoate and ethyl prop-2-enyl ether being observed in 4 h at 120 °C. In the absence of a catalyst, only low conversions were obtained. A plausible mechanism for this reaction is shown in Scheme 2.

Stoichiometric reactions

***(i)* Nature of the active species.** We have shown that under CO, [$Rh_2(OAc)_4$]·2MeOH reacts with excess PEt_3 to give [Rh(OAc)(CO)(PEt_3)$_2$] as a yellow oil.[24]

A reaction of [Rh(OAc)(CO)(PEt_3)$_2$] with a four-fold excess of 3-chloroprop-1-ene was monitored by ^{1}H and ^{31}P NMR spectroscopy (Table 2). At room temperature, the products are [RhCl(CO)(PEt_3)$_2$] and prop-2-enyl ethanoate, showing that the active species in the catalytic reactions is [RhX(CO)(PEt_3)$_2$], where X is the halide derived from the 3-halogenoprop-1-ene.



Scheme 2 Proposed mechanism for the production of prop-2-enyl ethanoate from 1-chloroprop-2-ene and sodium ethanoate catalysed by [Rh(OAc)(CO)(PEt_3)$_2$]

Table 2 Spectroscopic data for rhodium complexes[a]

	^{31}P		^{1}H[b]			
Complex	δ	J_{PRh}	=CH_2	=CH	Rh–CH_2	$\nu_{C\equiv O}$/cm^{-1}
[Rh(OAc)(CO)(PEt_3)$_2$]	25.3	126				1963s, 1710m[c]
[RhCl(CO)(PEt_3)$_2$]	24.5	117				1955s
[RhBr(CO)(PEt_3)$_2$]	22.5	120				1958s
[Rh(CH_2CH=CH_2)Cl_2(CO)(PEt_3)$_2$]	14.5	86	5.15 d (17), 4.90 d (10)	6.10 ddt (9, 10, 17)	2.75 bm	2049s, 1639w[d]
[Rh(CH_2CH=CH_2)Cl(OAc)(CO)(PEt_3)$_2$][e]	12.8	86				
[Rh(CH_2CH=CH_2)ClBr(CO)(PEt_3)$_2$][f]	12.2	85	5.12 d (17), 4.90 d (10)	6.12 ddt (10, 10, 17)	2.82 bm	
[Rh(CH_2CH=CH_2)BrCl(CO)(PEt_3)$_2$][f]	11.3	85	5.10 d (17), 4.88 d (10)	6.12 ddt (10, 10, 17)	2.90 bm	
[Rh(CH_2CH=CH_2)Br_2(CO)(PEt_3)$_2$]	8.8	85	5.12 d (17), 4.90 d (10)	6.12 ddt (10, 10, 17)	2.92 bm	
[Rh(*Z*-CH_2CH=Me)Cl_2(CO)(PEt_3)$_2$]	14.7	86	*g*,*h*	*g*	2.85 bm	
[Rh(*E*-CH_2CH=Me)Cl_2(CO)(PEt_3)$_2$]	14.4	86	5.75 m[h]	5.62 m	2.77 bm	
[Rh($COCH_2$CH=CH_2)Cl_2(CO)(PEt_3)$_2$]	19.3	67			3.10 d (7)[i]	2074s, 1764w,[d] 1633w[d]
[Rh($COCH_2$CH=CH_2)ClBr(CO)(PEt_3)$_2$][f,j]	16.9	71	5.38 d (17), 5.20 d (10)	5.90 ddt (10, 10, 17)	3.22 d (7)	
[Rh($COCH_2$CH=CH_2)BrCl(CO)(PEt_3)$_2$][f,j]	14.1	71	5.30 d (17), 5.25 d (10)	*g*	3.18 d (7)	
[Rh($COCH_2$CH=CH_2)Br_2(CO)(PEt_3)$_2$]	9.7	73	5.30 d (17), 5.20 d (10)	5.90 ddt (10, 10, 17)	3.25 d (7)	
[RhCl($CO)_2$(PEt_3)$_2$]	24.1	118				1992w, 1936s[k]
[RhBr($CO)_2$(PEt_3)$_2$][l]	40.4	69				1998w, 1939s[k]
[RhBr($CO)_2$(PEt_3)$_2$][l]	35.4	84				

[a] The NMR spectra in CD_2Cl_2 at 25 °C, IR spectra in Nujol mulls, unless otherwise stated. [b] Ordering as δ, multiplicity (J_{HH} Hz). [c] $\nu_{C\equiv O}$. [d] $\nu_{C\equiv C}$. [e] Cl *trans* to propenyl. [f] One has Cl *trans* to propenyl, other has Br *trans* to propenyl, arbitrary assignments. An unidentified doublet is also present in the spectrum (δ 13.0, J_{RhP} = 73 Hz). [g] Obscured by other resonances. [h] Assignment =CHMe (*Z* isomer) δ 1.52 d (8), (*E* isomer) 1.62 d (8). [i] 75 °C. [j] 90 °C. [k] In CH_2Cl_2. [l] −120 °C.

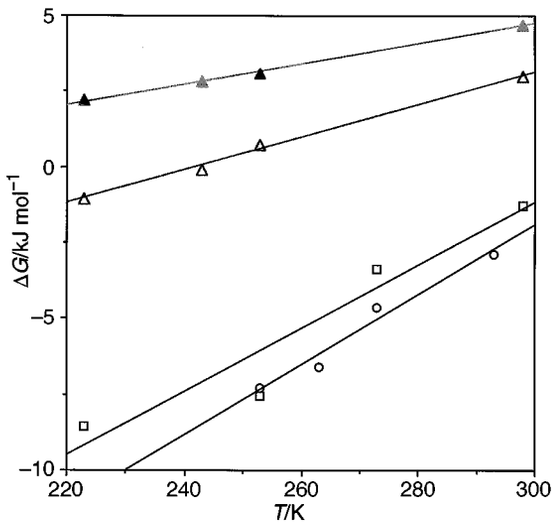


Fig. 2 Plots of ΔG against T for the oxidative addition of 1-chloroprop-2-ene (○); 3-chlorobut-1-ene (□); *Z*-1-chlorobut-2-ene (△) and *E*-1-chlorobut-2-ene (▲) to $[RhCl(CO)(PEt_3)_2]$

Table 3 Thermodynamic data for oxidative addition of allylic chlorides to $[RhCl(CO)(PEt_3)_2]$

Substrate	K_{253}/dm^3 mol^{-1}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
2-Chloroprop-1-ene	32	−36.0	−34.0
3-Chlorobut-1-ene	36	−32.0	−36.0
Z-1-Chlorobut-2-ene	0.7	−13.2	−104.0
E-1-Chlorobut-2-ene	0.23	−5.3	−115.0

Monitoring the reaction between $[Rh(OAc)(CO)(PEt_3)_2]$ and 3-chloroprop-1-ene by ^{31}P NMR spectroscopy at low temperature showed the presence of two Rh^{III} complexes. One is $[Rh(CH_2CH{=}CH_2)Cl_2(CO)(PEt_3)_2]$ (see below) whilst the other is tentatively assigned as the initial oxidative addition product, $[Rh(CH_2CH{=}CH_2)(OAc)Cl(CO)(PEt_3)_2]$.

***(ii)* Activation of the substrate.** In order to obtain information on the mechanism of the carbonylation reactions and especially on the reasons for the formation of the same products from either 1-chlorobut-2-ene or 3-chlorobut-1-ene, we have studied the reactions of $[RhCl(CO)(PEt_3)_2]$ with propenyl halides by variable-temperature NMR spectroscopy.

At −20 °C, $[RhCl(CO)(PEt_3)_2]$ reacts with a four-fold excess of 3-chloroprop-1-ene to give a rhodium(III) complex for which the η^1-prop-2-enyl structure $[Rh(CH_2CH{=}CH_2)Cl_2(CO)(PEt_3)_2]$ can be assigned from the NMR spectroscopic parameters (Table 2). Attempts to isolate this complex were frustrated by its thermal lability, but careful removal of all the volatiles at low temperature gives a yellow product which contains *ca.* 5:1 $[Rh(CH_2CH{=}CH_2)Cl_2(CO)(PEt_3)_2]$:$[RhCl(CO)(PEt_3)_2]$. On warming the NMR solution containing 1:4 $[RhCl(CO)(PEt_3)_2]$:$CH_2{=}CHCH_2Cl$ to room temperature, the ^{31}P NMR signal from the oxidative addition product decreases in intensity whilst that from $[RhCl(CO)(PEt_3)_2]$ increases. Quantitative studies were carried out on a solution containing $[RhCl(CO)(PEt_3)_2]$:$CH_2{=}CHCH_2Cl$ (1:0.82) at a variety of different temperatures. The equilibrium constant for the oxidative addition reaction at each temperature was calculated and used to evaluate ΔG. A plot of ΔG against T (Fig. 2) was used to evaluate the thermodynamic parameters shown in Table 3.

In order to know how the equilibrium constant for oxidative addition was affected by the halide, the oxidative addition of 3-bromoprop-1-ene to $[RhCl(CO)(PEt_3)_2]$ was also studied by ^{31}P NMR spectroscopy. At −40 °C, four Rh^{III} and two Rh^{I} complexes were present. These could be identified by the expected trends in chemical shift or by comparison with authentic samples as $[RhX(CO)(PEt_3)_2]$ and $[Rh(CH_2CH{=}CH_2)XY(CO)(PEt_3)_2]$ (X, Y = Cl or Br). As expected, the various complexes are in equilibrium, but the overall concentration of oxidative addition products at a given temperature is higher than that for 3-chloroprop-1-ene. On warming the solution, the relative concentrations of the various species alter (Table 3) with the Rh^{I} complexes being favoured at higher temperature and both $[RhBr(CO)(PEt_3)_2]$ and $[Rh(CH_2CH{=}CH_2)Br_2(CO)(PEt_3)_2]$ being favoured over their chloro analogues.

We have carried out similar reactions between $[RhCl(CO)(PEt_3)_2]$ and 3-chlorobut-1-ene or 1-chlorobut-2-ene, in order to discover more detail of the oxidative addition process and to explain the catalytic reaction products. With 3-chlorobut-1-ene, only one product (91% of Rh species present) is obtained and the equilibrium constant for its formation at −20 °C is 36.0 dm^3 mol^{-1}. For 1-chlorobut-2-ene, two products are obtained (19% of the total rhodium species present) at −50 °C. The major one is the same as that obtained from 3-chlorobut-2-ene, and corresponds to the oxidative addition product of the *E* isomer, whilst the minor one arises from oxidative addition of the *Z* isomer. The oxidative addition product is enriched in the *Z* isomer (*E*:*Z* = 1.6:1), relative to 6:1 in the free 1-chlorobut-2-ene. The equilibrium constants at −20 °C for the oxidative additions in this case are $K_Z = 0.7$ and $K_E = 0.23$ dm^3 mol^{-1},* much lower than for 3-chlorobut-1-ene. Examination of the ^{1}H and ^{31}P NMR spectra shows that on warming to 0 °C, all equilibria are shifted away from the oxidative addition products. Plots of ΔG against T are shown in Fig. 4 and thermodynamic parameters for the oxidative addition reactions in Table 3. For the reaction with 1-chlorobut-2-ene, the organic species present in solution at all temperatures up to 0 °C is 1-chlorobut-1-ene, although isomerisation to 3-chlorobut-1-ene (25%) occurs on standing overnight at 25 °C. For reactions starting from 3-chlorobut-1-ene, a trace of 1-chlorobut-2-ene (5% of the 3-chlorobut-1-ene) is present at −20 °C. On warming, reductive elimination leads to an increased amount of organic products and the relative ratio of 3-chlorobut-1-ene:1-chlorobut-2-ene remains at *ca.* 20:1 (*E*:*Z* = 6:1). Finally, almost no reaction occurs if the reaction of $[RhCl(CO)(PEt_3)_2]$ with 3-chlorobut-1-ene is carried out in toluene.

***(iii)* C–C bond formation.** In order to study the C–C bond forming reactions, we monitored the reaction of the oxidative addition products, $[Rh(CH_2CH{=}CH_2)XY(CO)(PEt_3)_2]$, with CO by high-pressure infrared and high-pressure NMR spectroscopies.

A 0.95:1 mixture of $CH_2CH{=}CH_2Cl$ and $[RhCl(CO)(PEt_3)_2]$ at −40 °C contains both $[RhCl(CO)(PEt_3)_2]$ and $[Rh(CH_2CH{=}CH_2)Cl_2(CO)(PEt_3)_2]$ (see above). No change is observed at this temperature when the NMR tube is pressurised with CO (40 bar). On warming, apart from the expected changes in the relative intensities of the signals from $[RhCl(CO)(PEt_3)_2]$ (increasing) and $[Rh(CH_2CH{=}CH_2)Cl_2(CO)(PEt_3)_2]$ (decreasing), a new signal begins to be apparent in the ^{31}P NMR spectrum at δ 19.3, $J_{PRh} = 73$ Hz. This increases in intensity as the temperature is raised and at 90 °C has an intensity *ca.* 50% that of the signal associated with $[RhCl(CO)(PEt_3)_2]$ (see below). On further standing at room temperature for 24 h, the resonance at δ 19.3 is the major resonance in the spectrum. Smaller (≈10–15%) doublets (δ 16.5, $J_{PRh} = 85$; 17.0, $J_{PRh} = 75$ Hz, unassigned) are also formed, the resonance associated with $[RhCl(CO)(PEt_3)_2]$ has almost disappeared and $[Rh(CH_2CH{=}CH_2)Cl_2(CO)(PEt_3)_2]$ accounts for *ca.* 10% of the rhodium-containing

* If this reaction is carried out by mixing at room temperature and cooling, there is some isomerisation (10%) to 3-chlorobut-1-ene and oxidative addition of this dominates so that the *E*:*Z* ratio is much higher (7.5:1 at – 40 °C with almost no free 3-chlorobut-1-ene remaining).

species. At the same time, the broad multiplet in the ^{1}H NMR spectrum from the Rh-bound CH_2 group (δ 2.72) is replaced by a sharper doublet at δ 3.08. In addition to these changes, a broad doublet appears in the ^{31}P NMR spectrum at δ 25 in the spectrum measured at 75 °C {in addition to the doublet from $[RhCl(CO)(PEt_3)_2]$}. At 90 °C this doublet is the major resonance in the spectrum, it is sharper than at 75 °C and is the only resonance near δ 25. We have shown in separate experiments that this resonance arises from a reaction of $[RhCl(CO)(PEt_3)_2]$ directly with CO (see below).

Monitoring the same reaction by high-pressure IR spectroscopy, but using excess (50 equivalents) 3-chloroprop-1-ene to enhance the amount of oxidative product present, a spectrum taken at 120 °C in the absence of CO showed predominantly the oxidative addition product (ν_{CO} 2049, $\nu_{C=C}$ 1639 cm^{-1}), together with $[RhCl(CO)(PEt_3)_2]$ (ν_{CO} 1955 cm^{-1}). On pressurising to 40 bar with CO, two new absorptions at 1992w and 1936s cm^{-1} were observed. All the other peaks decreased in intensity. On heating, new peaks at 2074, 1764 (very broad and contains peaks at 1639, 1764 and 1798 cm^{-1}) appeared, the peak at 2049 cm^{-1} from the oxidative addition product disappeared and the most intense peak was that at 1936 cm^{-1}. Attempts to prepare the proposed insertion product by oxidative addition of 3-chloropent-1-ene to $[RhCl(CO)(PEt_3)_2]$ were frustrated by the extreme lability and air sensitivity of the acyl product, however, NMR spectroscopic studies confirmed that this product was identical to those observed in the reaction of $[Rh(CH_2CH{=}CH_2)Cl_2(CO)(PEt_3)_2]$ with CO.

The mixture obtained from $[RhCl(CO)(PEt_3)_2]$ and 3-bromoprop-1-ene (see above) was also treated with CO. Once again, no reaction occurred at ambient temperature. On heating, broad resonances (sharpening at higher temperature) appeared in place of the resonances from $[RhX(CO)(PEt_3)_2]$ (X = Cl or Br) and the resonances from the oxidative addition products were replaced by other rhodium(III) doublets. These are tentatively assigned to CO insertion products and this assignment is supported by ^{1}H NMR spectroscopic studies which show that the broad multiplets near δ 2.87 from the Rh bound CH_2 groups were replaced by four doublets between δ 3.1 and 3.3. Tentative assignments of the ^{31}P resonances to the various insertion products are shown in Table 2. Those of $[Rh(COCH_2CH{=}CH_2)X_2(CO)(PEt_3)_2]$ (X = Cl or Br) have been confirmed by carrying out a similar sequence of reactions for $[RhX(CO)(PEt_3)_2]$ with $CH_2{=}CHCH_2X$.

***(iv)* Product formation.** Treating $[RhCl(CO)(PEt_3)_2]$ with $CH_2{=}CHCH_2Cl$ and CO (4 bar) in the absence of solvent at 100 °C produces a dark orange oil, insoluble in excess $CH_2{=}CHCH_2Cl$. Evaporation of excess $CH_2{=}CHCH_2Cl$ produced an orange, foul-smelling (but-3-enoic acid), highly air sensitive oil which could not be crystallised. The NMR spectroscopic studies showed it to be identical to the product obtained in the analagous NMR experiments (*i.e.* the acyl complex). On addition of ethanol, $[RhCl(CO)(PEt_3)_2]$ and ethyl but-3-enoate were smoothly produced.

***(v)* Reaction of $[RhX(CO)(PEt_3)_2]$ with CO.** The ^{31}P NMR and IR studies of reactions of solutions containing $[RhX(CO)(PEt_3)_2]$ with CO suggested that a direct reaction between them might occur. We therefore studied these reactions in the absence of other substrates.

On reaction with CO, both $[RhX(CO)(PEt_3)_2]$ (X = Cl or Br) react to give new species each with two absorptions in the C≡O stretching region of the IR spectrum (Table 2). For X = Cl, detailed IR studies were carried out at room temperature under various pressures of CO. The amount of the product with ν_{CO} at 1992 and 1936 cm^{-1} increases with p_{CO}, as shown in Fig. 3. The amount of this product decreases as the temperature increases under a constant pressure of CO (Fig. 4). These processes were both reversible.

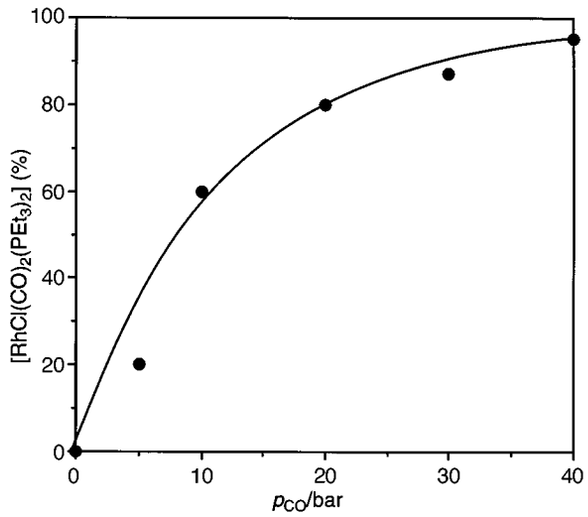


Fig. 3 Effect of p_{CO} on the relative amounts of $[RhCl(CO)_2(PEt_3)_2]$ and $[RhCl(CO)(PEt_3)_2]$ expressed as the percentage ratio of the intensity of the peak at 1992 cm^{-1} relative to the sum of the intensities of the IR absorptions at 1992 and 1955 cm^{-1}, T = 298 K

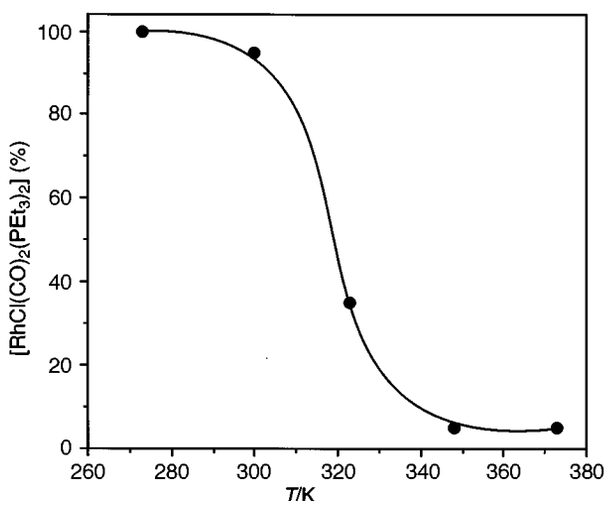


Fig. 4 Effect of T on the relative amounts of $[RhCl(CO)_2(PEt_3)_2]$ and $[RhCl(CO)(PEt_3)_2]$ expressed as the percentage ratio of the intensity of the peak at 1992 cm^{-1} relative to the sum of the intensities of the IR absorptions at 1992 and 1955 cm^{-1}, p_{CO} = 40 bar.

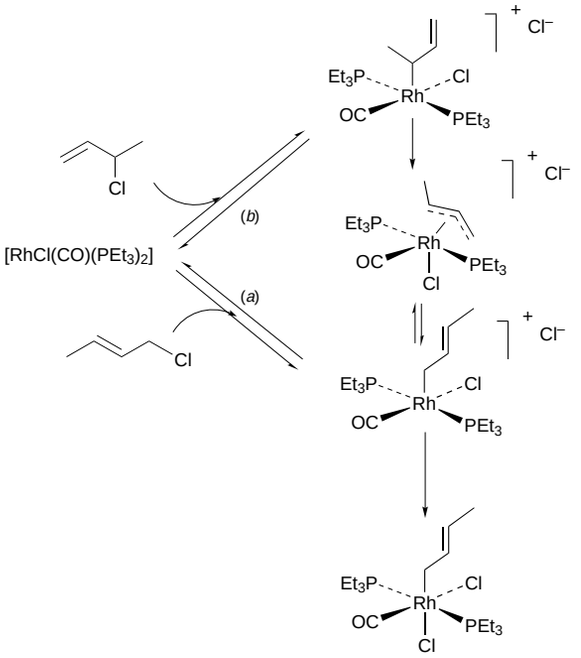
Both complexes give a single doublet in the ^{31}P NMR spectrum in the absence of CO. Under CO (40 bar) at room temperature, $[RhBr(CO)(PEt_3)_2]$ shows a broad doublet. On cooling, this broadens to a broad singlet and then separates into two doublets at δ 39.1 and 34.5 at −70 °C. At lower temperature, the relative intensity of these doublets changes, with that at δ ≈40 increasing.

Carbon-13 NMR studies were carried out on the reaction of $[RhX(CO)(PEt_3)_2]$ with excess CO (40 bar). At room temperature, a singlet was observed at δ 189.7 (X = Cl) or 190 (X = Br). At −100 °C for X = Cl, the singlet resolved into two doublets of triplets at δ 188.3 and 191.8 (relative intensity 2 : 1). For X = Br, only one doublet of triplets (δ 190) was observed at −100 °C.

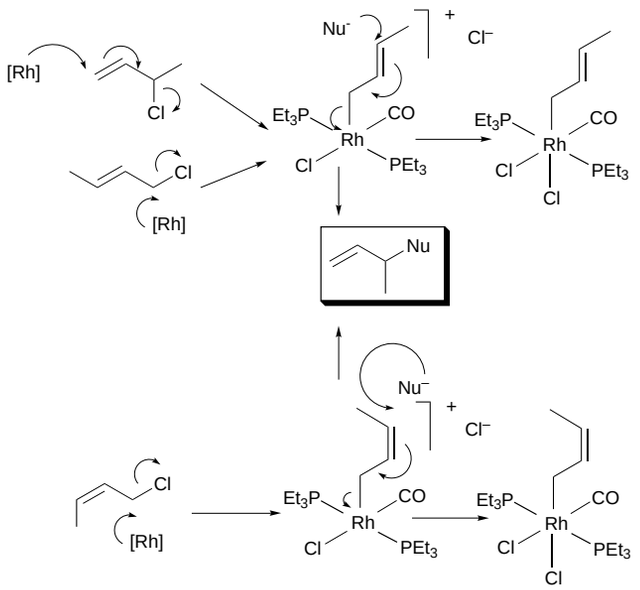
Discussion

Catalytic reactions

Stoichiometric studies show that the active species in the carbonylation of 3-halogenoprop-1-enes is $[RhX(CO)(PEt_3)_2]$ where X is a halide derived from the substrate. Oxidative addition of the substrate occurs rapidly even at low temperature but the equilibrium constant for the oxidative addition is relatively low. Since the reaction involves addition of two reactant molecules



Scheme 3 Possible mechanism for the formation of $[Rh(CH_2CH{=}CHMe)Cl_2(CO)(PEt_3)_2]$ from $[RhCl(CO)(PEt_3)_2]$ and either *E*-1-chlorobut-2-ene or 3-chlorobut-1-ene involving η^3 co-ordination of the butenyl ligand



Scheme 4 Proposed mechanism for the formation of $[Rh(CH_2CH{=}CHMe)Cl_2(CO)(PEt_3)_2]$ from $[RhCl(CO)(PEt_3)_2]$ and 1-chlorobut-2-ene (S_N2) or 3-chlorobut-1-ene (S_N2') and for the production of 3-ethoxybut-1-ene in the catalytic reaction carried out in ethanol. Nu = Cl or EtO

to give one product molecule, the negative ΔS° is as expected and accounts for the decrease in the amount of oxidative addition product as the temperature is raised. At the catalytic reaction temperature (120 °C) only a small amount of the oxidative addition product will be present even when the substrate is available in a large excess.

More detailed information about the exact mechanism of the oxidative addition reaction is available from the study of the oxidative addition of 1-chlorobut-2-ene and of 3-chloro-but-1-ene. These substrates both give the linear oxidative addition product, $[Rh(CH_2CH{=}CHMe)Cl_2(CO)(PEt_3)_2]$. This reaction has precedent in the oxidative addition of the same two substrates to $[RhCl(CO)\{PMe_2(2\text{-}MeOC_6H_4)\}_2]$ which both give the same (linear) product.[26] The fact that in our system the *E* : *Z* ratio is different for the two oxidative addition products shows that they do not form through a common intermediate. This rules out mechanisms that involve free 1-methylpropenyl radicals, cations or anions since C–C bond rotation in these species is expected to be sufficiently fast that the *E* : *Z* ratio in the oxidative addition product should be determined by thermodynamics and should be the same regardless of which substrate is employed.

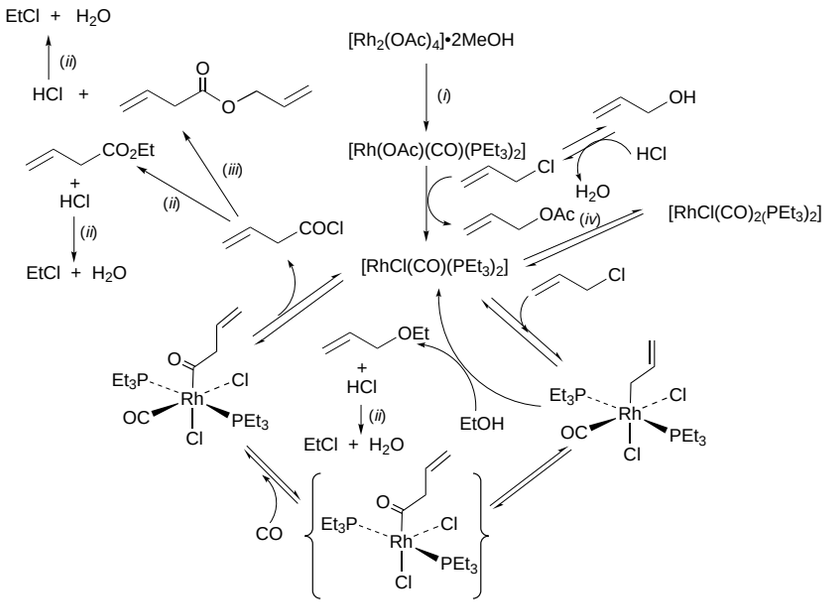
In general, oxidative additions of alkyl halides to rhodium(I) have been shown to occur by an S_N2 type of mechanism[26,27] and that appears to be the case in this system since almost no oxidative addition product is observed in toluene, which has little ability to solvate and stabilise the ionic intermediates. A straight S_N2 mechanism would lead to the observed product for 1-chlorobut-2-ene but not for 3-chlorobut-l-ene, where the first formed product should be $[Rh(CHMeCH{=}CH_2)Cl_2(CO)(PEt_3)]$. There are two possible mechanisms for the formation of the observed product.

In the first, shown in Scheme 3, the η^1-propenyl complex formed initially from S_N2 attack on the carbon atom attached to the halogen is a five-co-ordinated 16-electron cation. This rearranges to the 18-electron η^3-propenyl complex. Attack of Cl^- onto this 18-electron complex then occurs with the propenyl group becoming η^1 by unco-ordinating the double bond that gives the least sterically hindered product. Both 16-electron η^1-propenyl complexes should become η^3 but the *E* : *Z* ratio in the two η^3-propenyl complexes may be different because there is never free rotation about the CH=CHMe bond in the isomer derived from 1-chlorobut-2-ene. The stereochemistry of the product is then determined by that of the substrate. For the product derived from 3-chlorobut-1-ene, the stereochemistry will be determined during the formation of the η^3-propenyl intermediate. Our results do require that the η^3-propenyl derived from *Z*-1-chlorobut-2-ene always opens by decomplexation of the more substituted double bond since decomplexation of $CH{=}CH_2$ would lead to free rotation about the C–CHMe bond and only the *Z* oxidative addition product would be observed for both substrates. In related palladium-catalysed systems where 3-chlorobut-1-ene and 1-chlorobut-2-ene both give the straight chain acid chlorides it has been shown that η^3-propenyl intermediates are important.[28]

An alternative explanation, which would also account for the observed findings, is that attack of the rhodium-based nucleophile occurs *via* an S_N2 mechanism for the 1-chlorobut-2-ene but by an S_N2' process for 3-chlorobut-1-ene (Scheme 4). Both mechanisms have been shown to operate for simple organic nucleophiles on allylic halides with S_N2' being favoured by large nucleophiles and substitution on the C atom attached to the halide.[29] In our system, 3-chlorobut-1-ene bears a methyl group on the C atom attached to Cl and the rhodium-based nucleophile is certainly very large.

The only evidence that allows us to distinguish between the two mechanisms arises from warming the solution obtained from $[RhCl(CO)(PEt_3)_2]$ and 3-chlorobut-1-ene (1 : 1.14) up from −40 °C. At −40 °C the oxidative addition product, *Z*-$[Rh(CH_2CH{=}CHMe)Cl_2(CO)(PEt_3)_2]$ accounts for ≈92% of the rhodium present in solution (all of the Rh^{III}). At 25 °C, this complex is still present but the ratio of it to $[RhCl(CO)(PEt_3)_2]$ is 0.63 : 1. The organic product present at this stage is mainly 3-chlorobut-1-ene with *ca.* 5% 1-chlorobut-2-ene (*E* : *Z* = 6 : 1). That is, reductive elimination from $[Rh(CH_2CH{=}CHMe)Cl_2(CO)(PEt_3)_3]$ produces mainly $CH_2{=}CHCH(Me)Cl$.

Assuming that the principle of microscopic reversibility holds, the η^1–η^3 mechanism of Scheme 3 requires that the reductive elimination of the halide should occur by nucleophilic attack of Cl^- on the co-ordinated C atom of an η^1-propenyl group in a five-co-ordinate cation [reaction (*a*) or (*b*) in Scheme 3]. For the formation of 3-chlorobut-1-ene, this would require that attack of Cl^- upon $[Rh(CHMeCH{=}CH_2)Cl(CO)(PEt_3)_2]^+$, a precursor which is not detectable, occurs at a rate many times



Scheme 5 Proposed mechanism for the production of ethyl but-3-enoate and ethyl prop-2-enyl ether from 1-chloroprop-2-ene or prop-2-en-1-ol and CO in ethanol catalysed by $[RhCl(CO)(PEt_3)_2]$. Only the species in brackets has not been identified spectroscopically; (*i*) PEt_3, CO, EtOH; (*ii*) EtOH; (*iii*) prop-2-en-1-ol; (*iv*) CO

faster than attack upon $[Rh(CH_2CH{=}CHMe)Cl(CO)(PEt_3)_2]^+$, which is derived directly from the only Rh^{III} species present. The extra steric hindrance caused by the methyl group on the C atom of the 1-methylprop-2-enyl intermediate attached to rhodium makes this extremely unlikely and effectively rules out the η^1–η^3 propenyl mechanism. In contrast, if the S_N2/S_N2' explanation is correct, the reductive elimination could proceed *via* S_N2 or S_N2' attack of Cl^- onto the 16-electron, five-co-ordinated cation $[Rh(CH_2CH{=}CHMe)Cl(CO)(PEt_3)_2]^+$. An S_N2' attack would lead to 3-chlorobut-1-ene (the observed product) and might be expected because of the large bulk of the rhodium substituent (see Scheme 4). We thus favour the view that the oxidative addition proceeds *via* S_N2 or S_N2' mechanisms depending upon the substitution pattern of the substrate. The catalytic carbonylation product is determined by the oxidative addition step with both 3-chlorobut-1-ene and 1-chlorobut-2-ene giving the same product (ethyl pent-3-enoate). We note that both *Z* and *E* isomers are obtained from 3-chlorobut-1-ene in contrast to what is expected as a result of the oxidative addition reactions. This presumably arises because isomerisation of the double bond can occur at the much higher temperatures of the catalytic reaction. Indeed, in the stoichiometric reactions, isomerisation between 3-chlorobut-1-ene and 1-chlorobut-2-ene is observed at 25 °C.

On heating, CO inserts slowly into the η^1-propenyl rhodium(III) oxidative addition products to give the expected acyl intermediates, which can also be formed by oxidative addition of the appropriate acyl chloride across $[RhCl(CO)(PEt_3)_2]$ and for which the spectra are as expected (Table 2).

The high-pressure IR spectrum of $[RhCl(CO)(PEt_3)_2]$ in CH_2Cl_2, in the presence of excess 2-chloroprop-1-ene and CO (40 bar, 120 °C) shows weak features in the 1600–1800 cm^{-1} region at 1639, 1764 and 1798 cm^{-1}. The absorptions at 1639 and 1764 cm^{-1} can be assigned to $\nu_{C=C}$ and $\nu_{C=O}$ of the acyl complex respectively but that at 1798 cm^{-1} appears to be more consistent with appearance of free but-3-enoyl chloride ($\nu_{C=O}$ of an authentic sample is at 1802 cm^{-1}), suggesting that reductive elimination of the acid chloride may occur spontaneously, although in the catalytic reaction, direct attack of ethanol on the co-ordinated but-3-enoyl group is also possible. We have shown [17] that acetyl iodide spontaneously reductively eliminates from $[Rh(COMe)I_2(CO)(PEt_3)_2]$ provided that excess MeI is present to trap the $[RhI(CO)(PEt_3)_2]$ formed.

In dichloromethane, the reduction elimination reaction is reversible but in ethanol the acid halide immediately reacts to give ethyl butenoates and HX, which in turn reacts with ethanol to give EtX. The full mechanism for the formation of the various catalytic products is shown in Scheme 5.

An unusual feature of this system is that it is tolerant of both the HX and the EtX produced so that no added base is required to remove HX. This contrasts with most other systems and may be the reason why the amount of isomerised product, ethyl but-2-enoate, is lower than in most other systems, since it has been reported that this isomerised product is formed by a base catalysed reaction.[30,31]

The other product obtained in the catalytic reactions is a propenyl ether. There is a non-catalysed pathway to this product but the major pathway involves catalysis by the rhodium centre. Evidence for this comes from the higher yield of ether obtained in the presence of the catalyst and from the fact that both 3-chlorobut-1-ene and 1-chlorobut-2-ene produce the same ether, 3-ethoxybut-1-ene in the catalytic reaction, whereas direct reactions of the substrates with sodium ethoxide produce 3-ethoxybut-1-ene and ethyl but-2-enyl ether respectively [showing incidentally that the small ethoxide nucleophile attacks both substrates by an S_N2 (not S_N2') mechanism].

Since both substrates produce the same oxidative addition product, it is not surprising that they should catalyse the formation of the same ether. However, a simple S_N2 attack on the co-ordinated C atom would lead to ethyl but-2-enyl ether, which is hardly produced. The most likely mechanism for the formation of the ether, in the light of the discussion above, is an S_N2' attack of ethanol onto the co-ordinated η^1 but-2-enyl group, either in the six-co-ordinated complex or in a five-co-ordinate cation formed by loss of Cl^- (see Scheme 4). The slight decrease in the amount of ether produced with time at longer reaction times for 3-chloroprop-1-ene (Fig. 1) presumably means that the ether can also react with HCl to regenerate the halide and ethanol.

The products obtained from 1,4-dichlorobut-2-ene are not the expected diesters but rather the same as those obtained from 3-chlorobut-1-ene. A possible mechanism for this reaction involves rhodium-catalysed loss of Cl_2 to give butadiene followed by addition of HCl to generate 3-chlorobut-2-ene which then carbonylates. If this is the case, it is surprising that the catalyst is not poisoned by oxidative addition of Cl_2 to form $[RhCl_3(CO)(PEt_3)_2]$.

When using 3-chloroprop-1-ene in prop-2-en-1-ol as solvent, the reaction is much more selective towards the carbonylation product. The higher selectivity suggests that CO insertion into

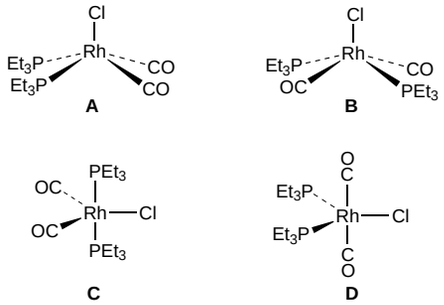


Fig. 5 Possible products from the reaction of $[RhX(CO)(PEt_3)_2]$ with CO

the Rh–C bond of the η^1 propenyl complex competes more effectively with S_N2' attack of the alcohol than when the alcohol is ethanol. This is consistent with the known lower nucleophilicity of prop-2-enol than of ethanol.[32] The mechanism for carbonylation of prop-2-en-1-ol is shown in Scheme 5.

Reaction of $[RhX(CO)(PEt_3)_2]$ with CO

Studies of the reaction of $[RhX(CO)(PEt_3)_2]$ (X = Cl or Br) with CO indicate that new products are formed. At very low temperatures, ^{31}P or ^{13}C NMR studies indicate that two different species each with equivalent P atoms and equivalent CO groups are formed. On warming these exchange with one another but free $[RhX(CO)(PEt_3)_2]$ is also formed. The singlet observed in the CO region of the ^{13}C NMR spectrum at 25 °C suggests that the co-ordinated CO group(s) are exchanging with free CO so that couplings to Rh and to P are lost. The temperature and pressure dependence of the relative amounts of $[RhCl(CO)(PEt_3)_2]$ and of the new species are consistent with the new species being $[RhCl(CO)_2(PEt_3)_2]$. For entropic reasons, the amount of this is expected to decrease as the temperature is increased. Fortunately, at 120 °C under 40 bar of CO, very little of the 18-electron five-co-ordinate species is present so that co-ordination of CO will not compete effectively with oxidative addition of the substrate during the catalytic reaction. High-pressure IR studies at room temperature and above show that the major five-co-ordinate species present has 2 ν_{CO}, one much stronger than the other. The combined IR, ^{13}C and ^{31}P NMR spectroscopic data suggest that the most likely structure of this compound is **B** or **C** (Fig. 5). The only structurally characterised example of a complex of formula $[MX(CO)_2P_2]$ (M = Rh or Ir) is $[IrCl(CO)_2(PPh_3)_2]$ obtained from $[IrCl(CO)(PPh_3)_2]$ and CO (**C** in Fig. 5).[33,34] This has a trigonal-bipyramidal structure with mutually *trans* phosphines and axial CO ligands. The IR spectrum shows ν_{CO} at 1923 and 1976 cm^{-1}. Iridium complexes containing $Ph_2ECH_2CH_2EPh_2$ (E = P or As)[35,36] with *cis*-E atoms (ν_{CO} 2048, 1962 cm^{-1}, E = P; 2050, 1965 cm^{-1}, E = As) are also known. The compound $[RhCl(CO)_2(NH_3)_2]$[37] has been reported, but it has been suggested that the complexes $[RhCl(CO)_2L_2]$ (L = $SbPh_3$ or pyridine) may have been wrongly formulated.[38]

Conclusion

We conclude that $[RhX(CO)(PEt_3)_2]$ (X = Cl, Br or I), added directly or prepared *in situ* from $[Rh_2(OAc)_4]\cdot 2MeOH$ and PEt_3 *via* $[Rh(OAc)(CO)(PEt_3)_2]$, is an effective catalyst for the carbonylation of allylic halides to esters of but-3-enoic acids with the major side products being ethers. Both 3-chlorobut-1-ene and 1-chlorobut-2-ene produce ethyl pent-3-enoate and 3-ethoxybut-1-ene. All the intermediates in the catalytic cycle have been spectroscopically characterised and the oxidative addition step has been shown to occur *via* S_N2 or S_N2' processes depending upon the steric requirements of the substrate. The ether-forming reaction probably involves S_N2' attack of ethoxide on an η^1 propenyl species. The reaction of CO with $[RhX(CO)(PEt_3)_2]$ (X = Cl or Br) has been shown to give two isomers of the 18-electron complex $[RhX(CO)_2(PEt_3)_2]$ which interconvert with one another and with $[RhX(CO)(PEt_3)_2]$ at higher temperatures.

Acknowledgements

We thank BP Chemicals and the EPSRC for a studentship (M. J. P.) and other funding (high-pressure IR cell). We are indebted to Professor M. J. Green and Dr. A. Poole for helpful discussions.

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Received 29*th April* 1997; *Paper* 7/02942J