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Catalytic applications of rhodium complexes containing trialkylphosphines[1]

Michael C. Simpson [2], David J. Cole-Hamilton *

School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, UK

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* Corresponding author.

[1] In honour of Professor K. Vrieze.

[2] Current address: BP Chemicals, Salt End, Hull HU12 8DS, UK.

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Abstract

The uses of trialkyl complexes of rhodium as homogeneous catalysts are reviewed. Although they have been much less studied than their triarylphosphine counterparts, rhodium trialkylphosphine complexes do have certain properties which make them suitable for a wide range of catalytic reactions, for some of which, they are the only systems available, or are the catalysts of choice. The major difference between complexes containing trialkylphosphines and those with triarylphosphines is that the electron donating trialkylphosphines lead to a much higher electron density on the metal and hence make oxidative addition reactions, even of difficult substrates, more facile. Examples of where this is particularly beneficial include the photocatalysed activation of alkanes, either to produce alkenes and H_2 or, in the presence of CO, to produce homologous aldehydes; the activation of amines in the hydroamination of alkenes; their ability to dehydrogenate alcohols, directly, via transfer of hydrogen to acceptors such as alkenes, or in hydrocarbonylation reactions where the alcohol is the hydrogen source; the water–gas shift reaction; their ability to catalyse the carbonylation of allylchlorides and CH_2I_2. Another example of the effect of the high electron density on the metal is the production of alcohols, rather than aldehydes as the primary products from alkenes under hydroformylation reaction conditions, which is believed to proceed via an hydroxycarbene complex formed by protonation of an acyl intermediate. The hydrogenation of CO catalysed by trialklyphosphine complexes of rhodium may also be possible because the high electron density on the rhodium makes a hydrido ligand sufficiently hydridic for it to be transferred to CO coordinated to another rhodium centre to form the crucial formyl intermediate.

In addition to these rather unusual reactions, trialkylphosphine complexes of rhodium also show activity for a variety of other more classical reactions, such as hydrogenation (especially of aldehydes and ketones), hydrosilylation, hydroboration and condensation reactions of alkenes and alkynes. For most of these reactions, apart from the hydrogenation of aldehydes, these catalysts tend to be inferior to their triarlyphosphine counterparts.

Keywords: Rhodium; Trialkylphosphine; Catalysis

1. Introduction

Some of the major recent advances in the manufacture of bulk, medium volume or even fine chemicals have utilised homogeneous transition metal complex catalysed reactions. Despite the problems that can be associated with the separation of the

products from the solvent and the catalyst, the very high activity and product selectivities that can be obtained have allowed some of these processes to be extensively exploited in industry.

Three examples of successful innovations of this kind involve rhodium-based systems; the extremely high activity, selectivity and stability of the catalysts being sufficient to overcome the very high cost penalty of using rhodium. These processes are the hydroformylation of alkenes using $[RhH(CO)(PPh_3)_3]$ [1a], the carbonylation of methanol using $[Rh(CO)_2I_2]^-$ [2] and the asymmetric hydrogenation of α-amidocinnamic acids used in the synthesis of α-dihydroxyphenylalanine (L-DOPA) for the control of the symptoms of Parkinson's disease [3].

Both the hydroformylation and asymmetric hydrogenation reactions involve the use of metal complexes containing arylphosphines (usually diphosphines in the asymmetric hydrogenation) so that extensive studies on the catalytic activity of such complexes have been carried out [1,3]. In contrast, the uses of alkylphosphine or diphosphine complexes of rhodium in catalysis have been much less comprehensively studied. In part, this was because in many of the early studies much lower selectivities and activities were observed for these complexes than for their counterparts containing arylphosphines [4]. The low activities could be attributed partly to the generally lower liability of the $Rh-RR_3$ (R = alkyl) bond, meaning that the creation of vacant sites on the rhodium could be difficult, and partly to the fact that the electron donating phosphines might be expected to stabilise rhodium(III) better than rhodium(I), whilst similar stabilities for the two oxidation states are required if a catalytic cycle is to involve both oxidation states. The handling of the liquid, air-sensitive and noxious trialkylphosphines is also rather more difficult than that for the triarylphosphines, which, as odourless solids, can be handled and stored in air.

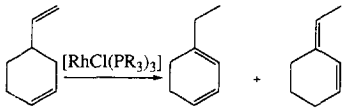
More recently, however, it has become apparent that some of these properties (particularly the electron donating ability of these trialkylphosphines) can be put to good use, and that there are certain reactions for which trialkylphosphine complexes of rhodium are the catalysts of choice. Amongst these, the most exciting and important is the catalytic activation of C—H bonds in simple alkanes to give alkenes by dehydrogenation [5] or aldehydes by carbonylation [6]. Other important reactions include the water–gas shift reaction (WGSR) [7] and the direct formation of alcohols from hydroformylation of alkenes under mild conditions (40 bar, 120 °C) [8]. Most hydroformylation reactions are directed towards the production of alcohols for plasticisers, soaps or detergents. Rhodium-based catalysts generally produce aldehydes so that a subsequent hydrogenation step is required [1]. Cobalt catalysts promoted by trialkylphosphines do produce alcohols but the conditions are very forcing (150–200 °C, 50–400 bar) [9].

In this review, we discuss the various homogeneous catalytic reactions for which trialkylphosphine complexes of rhodium can be used. The review is structured so that the degree of complexity of the reaction being catalysed increases towards the end.

2. Isomerisation reactions

Isomerisation is observed as a competing reaction in many rhodium–trialkylphosphine catalytic systems. Surprisingly there are only a few examples where these

systems are used for isomerisation alone. One is the catalysed isomerisation of vinylcyclohex-3-ene [10] in which a mixture of two products, both with conjugated double bonds, was obtained (Eq. (1)). Two catalysts were examined for this transformation, $[RhCl(PR_3)_3]$, (R = Ph (phenyl) or ^{i}Pr). P^iPr_3 gave the more active and selective catalyst.



(1)

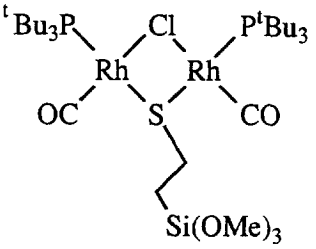
Using $[Rh_2Cl(SR)(CO)_2(P^tBu_3)_2]$ (R = alkyl or (un)substituted phenyl group, Bu = butyl) as the catalyst, 1-octen-3-ol, 4-allylanisole and *trans*-stilbene oxide can be isomerised into 3-octanone, *cis/trans*-4-(1-propenyl)anisole and deoxybenzoin respectively, often in 100% conversion [11]. $[RhCl(PMe_3)_3]$ catalyses the isomerisation of epoxides to aldehydes (ethene oxide) or ketones (styrene oxide or propene oxide [12,13]. $[RhHCl(CH_2COR)(PMe_3)_3]$ (R = Me or Ph) are isolated from the final solutions, suggesting that reductive elimination of the ketone is the rate determining step. Using ethene oxide the isolated rhodium species is $[RhHCl(COMe)(PMe_3)_3]$, probably formed from oxidative addition of product ethanal to the complex [12,13].

3. Hydrogenation

3.1. Hydrogenation of alkenes

Hydrogenation using triphenylphosphine rhodium compounds, especially Wilkinson's catalyst, $[RhCl(PPh_3)_3]$, is a well known process for alkenes [1a,b]. In contrast, very few hydrogenation reactions utilising trialkylphosphines have been reported in the literature.

Early publications compared different phosphines in the hydrogenation of cyclohexene. In these, PPh_3 was found to be 40 times more active than PEt_3 [14]. Similarly, for the hydrogenation of hex-1-ene using catalysts prepared *in situ* from $[Rh(cod)Cl]_2$ [15] (cod = 1,5-cyclooctadiene), $[Rh(C_2H_4)_2Cl]_2$ [15], $[RhCl(cot)_2]_2$ (cot = cyclooctene) [16] or [RhCl(butadiene)$_2$] [16], P(*p*-$MeOC_6H_4)_3$ (the most active added phosphine) was 20 times more active than PBu_3 [16]. A similar study using hept-1-ene as the substrate, but employing preformed $[RhCl(CO)(PR_3)_2]$ (R = Ph, OPh or Cy (cyclohexyl) showed that PCy_3 was superior to $P(OPh)_3$ but slightly less active than PPh_3 [17]. Using PPh_3, the reaction was complete after 3 h, producing 80% heptane and 20% *Z/E* hept-2-ene; the yield of heptane increased slowly after 3 h due to the very slow hydrogenation of hep-2-tene. Using PCy_3, the reaction was greater than 80% complete after 5 h, the product distribution being heptane ca. 75% and hept-2-ene ca. 25%. Using $P(OPh)_3$ the reaction was 10% complete after 5 h, the product ratios being similar to those obtained with the other phosphines.



I

$[RhH_2Cl(PCy_3)_2]$ is active for the hydrogenation of alkenes, particularly cod at 1 bar and 100 °C [18], whilst $[RhHCl_2(P^tBuPr_2)_2]$, in the presence of base, is as active as Wilkinson's catalyst for the hydrogenation of hex-1-ene [19]. Cationic rhodium complexes, such as $[RhH_2L_2]^+$ ($L = P^iBu_3$ or PMe_3) prepared *in situ*, have been studied for the partial hydrogenation of long chain dienes with a view to applying this methodology to fats and oils. PMe_3 containing systems hydrogenate *E* double bonds preferentially and P^iBu_3 *Z* double bonds. PMe_3 also isomerised the position of the remaining double bond to a greater extent than P^iBu_3. Using PMe_3, 60–70% of the dienes were converted to monoenes; the remainder were either fully hydrogenated or isomerisation products of the initial dienes [20]. Dimeric complexes such as **I** have been used for the hydrogenation of 3-octen-3-ol to 3-octanol [21].

3.2. Hydrogenation of nitriles

$[RhH(P^iPr_3)_3]$ and $[Rh_2H_2(\mu\text{-}H_2)(PCy_3)_4]$ were the first catalysts to show activity for the hydrogenation of nitriles at ambient temperature [22]. $[RhH(P^iPr_3)_3]$ (1 bar, 20 h) was especially active, giving 100% conversions with $Me(CH_2)_4CN$ and ^iPrCN. Aromatic groups directly attached to the nitrile made the transformation sluggish (45% conversion using $[RhH(P^iPr_3)_3]$), but substrates with nitrile groups not directly attached to the aromatic ring (e.g. $PhCH_2CN$) were notably more active. The system is not very selective for unsaturated nitriles, since hydrogenation of the C=C also occurs. At elevated temperatures (110 °C under a steady stream of nitrogen) both compounds served as dehydrogenation catalysts, to turn amines into nitriles, e.g. benzylamine was converted to benzonitrile (27%) in 24 h [22].

3.3. Hydrogenation of aldehydes and ketones

In contrast to alkene hydrogenation, trialkylphosphine–rhodium systems tend to be more effective (compared with the triarylphosphine–rhodium systems) in the hydrogenation of carbonyl groups. Aldehydes or ketones can therefore be hydrogenated to alcohols.

High yields of alcohols could be formed from a range of aldehydes using $[Rh(nbd)(PEt_3)_2]ClO_4$ (nbd = norbornadiene; Et = ethyl) dissolved in alcohols [23]. Between 79% and 97% conversion could be obtained from the aromatic aldehydes (e.g. benzaldehyde) and ca. 40% for aliphatic aldehydes.

Replacing PEt_3 with PMe_3 approximately halved the conversion [23,24], whilst PPh_3 gave negligible conversion, except when the aldehydic substrate, phenylacetaldehyde, was used. In this case, the conversion was 45.7% (cf. 47.8% for PMe_3 and 79.8% for PEt_3). Bis(diphenylphosphino)ethane inhibited reactions catalysed by $[Rh(nbd)(PEt_3)_2]ClO_4$.

Ketones could also be hydrogenated using these cationic catalysts [25] with conversions being in the range 47.6–100% (without much distinction between aromatic methyl ketones or aliphatic methyl ketones). The rate of reaction for aldehydes was nearly an order of magnitude higher than for ketones. One notable exception was methoxymethyl methyl ketone, which was hydrogenated at a similar rate to the aldehydes. This was attributed to the electron withdrawing effects of the methoxy group in the ketone [25].

Hydrogenation of unsaturated ketones show that C=C tended to be hydrogenated in preference to C=O. For instance, when methyl vinyl ketone was hydrogenated the C=C were completely hydrogenated within 0.5 h, whilst the carbonyl group was only 60% hydrogenated after 20 h, leaving 40% methyl ethyl ketone [25].

Using $[RhH(PEt_3)_3]$ pre-prepared or prepared *in situ* from $[Rh_2(OAc)_4]$ and PEt_3 (Ac = acetyl), aldehydes such as heptanal or 2-methylpropanal can be cleanly hydrogenated ($CO-H_2$, 40 bar, 120 °C) to give alcohols [8,26–28]. Alcoholic solvents such as ethanol were preferred. Reactions carried out using heptanal and D_2 in EtOH gave a mixture of $C_6H_{13}CHDOH/D$ and $C_6H_{13}CH_2OH/D$, whilst using D_2 in EtOD only $C_6H_{13}CD_2OD$ was formed. This suggests that two mechanistic cycles are operating, in one of which the alcoholic proton of the solvent is incorporated into the product. The two cycles proposed are shown in Fig. 1.

$[RhHCl_2(PCy_3)_2]$ is active for the hydrogenation (1 bar, 25 °C) of α,β-unsaturated aldehydes and ketones (the alkene being preferentially hydrogenated) [29] at 1 bar

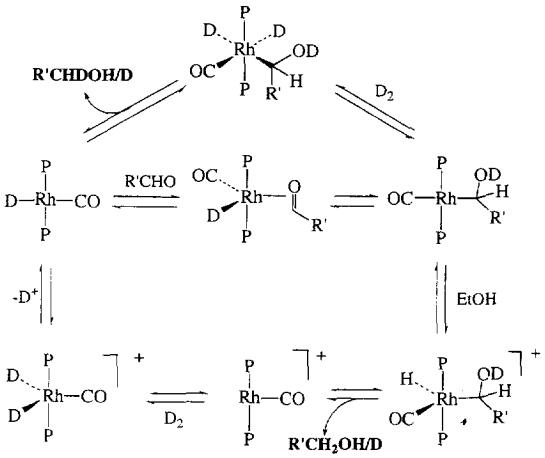


Fig. 1. Proposed mechanisms for the hydrogenation of aldehydes using D_2 catalysed by $[RhHP_3]$ in the presence of CO. Both labelling patterns for the product are observed. P = PEt_3, R' = C_6H_{13} or Me_2CH [8,26–28].

and 25 °C. Selectivities were high (generally 90–96% at 100% conversion), but promoters such as water (aldehydes) or NaOH(aq) (ketones) were necessary, and thus biphasic systems were formed. An attractive feature of this system is that $[RhHCl_2(PCy_3)_2]$ is easy to handle and air stable. Once activated it converts to $[RhH_2Cl(PCy_3)_2]$ (isostructural and isoelectronic with $[RhH_2Cl(PPh_3)_2]$, which is the active hydrogenation species in the Wilkinson's catalyst system) [1b].

Formaldehyde can be hydrogenated over $[Rh(CO)_2(acac)]$ (acac = 2,4,-pentanedionato) modified with PBu_3 (145 bar, 150 °C, 1 h) giving 73.9% MeOH at 100% conversion [30].

3.4. Asymmetric hydrogenation

Although rhodium-based catalysts are amongst the most successful for the asymmetric hydrogenation of α-amidocinnamic acids or esters [3], attempts to use rhodium trialkylphosphine complexes in which the chirality is on P, $\{(S)$-(+)-2-methylbutyl$\}_3P$ [31] or on a carboxylato ligand such as (+)-*N*-acetylphenylalanine in $[Rh(O_2CR^*)P_2]$ [32,33] have been rather unsuccessful, with enantiomeric excesses (e.e.) being generally less than 15%. For the carboxylate complexes, PMe_3 and POc_3 were the best phosphines tested giving e.e.s of 13% and 9.5% respectively, whilst phosphines containing aryl substituents generally gave less than 1% e.e. The hydrogenation of acetophenone using a cationic catalyst containing $\{(R)$-2-methylbutyl$\}_3P$ has also been attempted but the e.e. was less than 0.3% [34]. Similarly disappointing results have been obtained using rhodium(I) catalysts containing ligands of the form $Cy_2PCH_2N(R)CH_2PCy_2$ (R = CHMePh, CHMeCOOEt or bornyl) [35].

The effect of added trialkylphosphines on the hydrogenation of acetophenone catalysed by $[RhCl(nbd)]_2$ and (+)-diop (diop = 2,3-*O*-isopropylidene-2,3-hydroxy-1,4-bis(diphenylphosphino)butane) has been examined [36]. The optical yield of the *R*-(+)-alcohol was 51%. However, on addition of free trialkylphosphine (Rh:diop:PR_3, 1:1:1), the product became predominately *S*-(−)-alcohol (e.e. = 12%) (R = Bu or Pe). To examine this further the Σ P:Rh was held steady at either 2:1 or 3:1 and the ratio of diop:PR_3 varied. The results are shown graphically in Fig. 2.

The shape of the graph for a 2:1 P:Rh ratio is simple to explain. With no free phosphine available, two catalytic species are present, one giving an optical yield (diop), the other not (PR_3). The graph for the 3:1 P:Rh ratio is more complex, possibly indicating a third mixed phosphine species with one PR_3 and a monodentate diop. The free end of the diop causes a reverse in stereochemistry compared with the bidentate system.

The stereochemistry of hydrogenation of cyclic ketones (especially 4-t-butylcyclohexanone) has been examined in some depth [37]. Using $[RhCl(nbd)]_2$ with added PR_3 (R = Bu or Ph), predominantly *anti* alcohol was formed (slowly in the case of PPh_3). On addition of base (NEt_3), the system using PPh_3 started giving *syn*-alcohol, while the selectivity in the PBu_3 system remained unchanged. Preformed

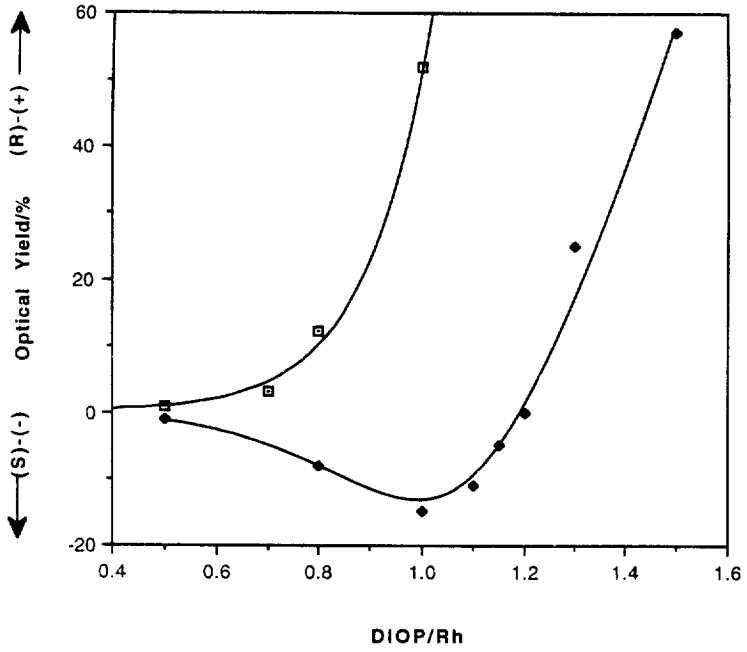


Fig. 2. The influence of added PBu_3 on the enantioselectivity of the asymmetric hydrogenation of acetophenone using a catalyst formed in situ from $[RhCl(nbd)]_2$ and (+)-DIOP. ⊡ ΣP:Rh = 2:1; ◆ ΣP:Rh = 3:1 [36].

$[HRh(PR_3)_4]$ gave *syn* alcohols using either phosphine. It was conjectured that the equilibrium shown in Eq. (2) ($x = 2$ or 3) was set up in the system.

$$[Rh^{III}H_2Cl(PR_3)_x] + B \rightleftharpoons [Rh^{I}H(PR_3)_x] + BH^+ + Cl^- \quad (2)$$

The reason for the change in selectivity appears to be the way that Rh^I, which binds the substrate for monohydridic catalysts, and Rh^{III}, responsible for substrate binding in dihydridic catalysts, coordinate to the intermediate formed by insertion of the aldehyde into the Rh—H bond. Rh^{III} binds to the hard O atom, so forming an alkoxy intermediate, whilst for Rh^I, an Rh—C bond is formed. In both cases, the bulky Rh complex occupies an equatorial site after H transfer. Thus, for 4-t-butylcyclohexanone, the pathways shown in Fig. 3 explain the stereochemistries of the observed products. The insensitivity of the stereochemistry of the product to the addition of NEt_3 when $[RhCl(nbd)]_2$ is used with PBu_3 suggests that the strongly electron donating PBu_3 ligands make the Rh—H bonds sufficiently hydridic that they are not deprotonated by NEt_3.

3.5. *Hydrogenation (ring opening) of epoxides*

Epoxides can be ring opened by hydrogenation (1 bar, 30 °C in aqueous diglyme, 3 h) using an ionic $[Rh(nbd)P_2][ClO_4]$ catalyst ($P = PEt_3$, PMe_3, PPh_3 or $P_2 =$

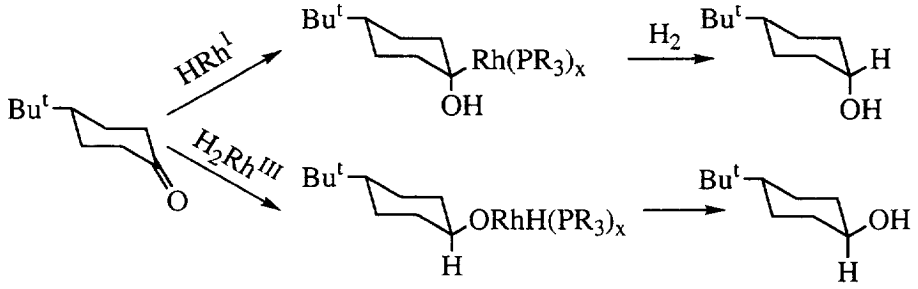
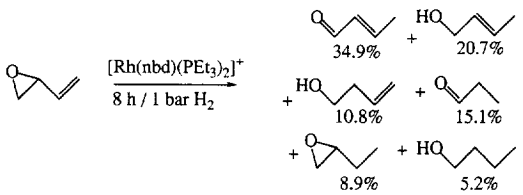


Fig. 3. Proposed rationalisation of different selectivities observed in the hydrogenation of 4-*t*-butylcyclohexanone using various catalysts. R = Bu or Ph [37].

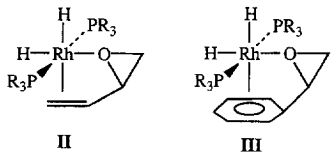
1,2-bis(diphenylphosphino)ethane). The two most successful reactions involved styrene oxide and 3,4-epoxybut-1-ene, both giving *anti* products [38,39]. Styrene oxide with PEt_3 gave 90% conversion to $PhCH_2CH_2OH$ (66%), $PhCH_2CHO$ (trace) and oligomers (22%). PMe_3 achieved only 40% conversion (alcohols : oligomers being ca. 1 : 1). PPh_3 and 1,2-bis(diphenylphosphino)ethane give 100% conversion, but in both cases greater than 50% of the yield was oligomers. 3,4-epoxybut-1-ene was 100% converted to the products shown in Eq. (3), in 8 h. Isomerisation and hydrogenation of the double bonds were competing reactions. Oligomers made up the rest of the products. In contrast, 1,2-epoxybutane only gave 0.65% conversion in 100 h.



(3)

It was proposed that successful ring opening was only achieved with epoxides for which a remote group in the molecule can stabilise the binding of the epoxides as in **II** or **III**, derived from 3,4-epoxybut-1-ene or styrene oxide respectively.

Catalytic ring opening of the four-membered ring of biphenylene to give biphenyl has also been achieved using hydrogenation (500 Torr, 85 °C) catalysed by $[Rh(C_5Me_5)H_2(PMe_3)]$, although only 7 turnovers were observed in 7 days [40].

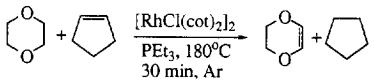


4. Transfer hydrogenation

Transfer hydrogenation involves the transfer of two hydrogen atoms from a donor molecule, often an alcohol or ether, to an acceptor molecule.

$[RhH(CO)L_3]$ ($L = PEt_3$, P^tBu_3, PEt_2Ph, $PMePh_2$) is capable of effecting hydrogen transfer from benzyl alcohol to terminal alkenes (normally oct-1-ene) in the presence of potassium benzoate. Turnovers of 35 in 4 h were recorded [41].

In a study of many metals (cobalt, rhodium, tantalum and iron to name but a few), with many ligands (mostly phosphines), it was found [42] that the best systems were generated *in situ* from $[RhCl(cot)_2]_2$ and PEt_3, PPr_3 or PBu_3 (4 equivalents). These catalysed transfer hydrogenation reactions with greater than 83% conversion (93% in the case of PPr_3) using 1,4-dioxane as the donor with cyclopentene being the acceptor (Eq. (4)).



(4)

A popular sacrificial donor employed is isopropanol. Rhodium-based catalysts again formed *in situ* from $[Rh_2(OAc_2)_4]$ [43], $[RhCl(cot)_2]_2$ [44] or $[RhCl(cod)]_2$ [45] and various phosphines showed the highest activity for the transfer hydrogenation of ketones or alkenes. Thus, catalysts prepared *in situ* from $[Rh_2(OAc)_4]$ [43] have been used to carry out hydrogen transfer from propan-2-ol to cyclohexanone. Rhodium acetate itself was inactive, but with nitrogen-based ligands conversions up to 88% (using 2,2′-bipyridyl) in 1 h were obtained. Tributylphosphine gave 40% conversion in the same time, whilst the yield using triphenylphosphine was only 28%.

Transfer hydrogenation of 4-t-butylcyclohexanone with $[RhCl(cod)]_2$ with various phosphines and a cocatalyst of KOH (in the ratio of KOH:Rh, 10:1), was carried out at 83 °C [44]. When PPh_3 was used a conversion of 97% (77% *syn* isomer) was achieved in 5 min. PCy_3 produced 98% (55% *syn*) in 120 min; P^tBu_3 gave 86% (49% *syn*) after 180 min. A large excess of phosphine inhibited the reaction. Alkene hydrogenation can be accomplished in the same catalytic system [44]. Rates are low, e.g. only 9% of cyclohexene had reacted to form cyclohexane in 180 min. Using unsymmetrical alkenes, it was shown that isomerisation was also occurring. 3-methylcyclohexene gave methylcyclohexane (30%) and 1-methylcyclohexene (60%) in 420 min. To investigate whether isomerisation was a prerequisite for the hydrogenation, 1-methylcyclohexene was examined as the initial substrate, only 5.5% had hydrogenated in 180 min, suggesting that isomerisation competes with, rather than precedes, hydrogenation. Analogous iridium-based catalysts were less effective [45].

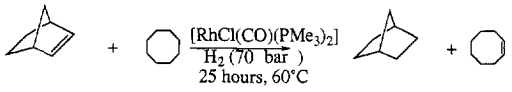
Further studies of the transfer hydrogenation of alkylcyclohexanones have demonstrated that when the alkyl group is in the 2 position, it has a major directing effect, forcing the *syn* isomer of the product to predominate. When the alkyl group was in the more distant 4 position the phosphine basicity was the greater factor influencing which isomer was the dominant product. PPh_3 favoured the *syn* product, whilst P^tBu_3 marginally favoured *anti* [45].

Complexes of the form $[\{RhH(PCy_3)_2\}_2(\mu\text{-}N_2)]$ and $[RhH(P^iPr_3)_3]$ are active catalysts for hydrogenation of ketones [46] or hex-1-ene [47] using either H_2 or ^{i}PrOH as the hydrogen source. Yields were 88–93% for H_2 and 35–99% for ^{i}PrOH for various substrates, e.g. PhCOPh, MeCOCOMe [46].

Compounds of formula $[Rh_2Cl(SR)(CO)_2(P^tBu_3)_2]$ (R = alkyl or (un)substituted phenyl group) can catalyse the transfer hydrogenation of α,β-unsaturated ketones using formic acid as the sacrificial hydrogen donor (Eq. (5)) [11].

$$C_6H_5CH{=}CHC(O)C_6H_5 + HCO_2H \xrightarrow[\substack{22\,h\\ toluene\\ 97\,^\circ C}]{cat.} C_6H_5CH_2CH_2C(O)C_6H_5 + CO_2 \tag{5}$$

Although many catalyst systems are active for transfer hydrogenation from donors such as secondary alcohols, there are fewer that can activate C—H bonds in alkanes so that the alkane acts as a hydrogen donor. Some of the most active systems for this kind of reaction are based on rhodium trialkylphosphine catalysts. These reactions are related to the photochemical dehydrogenation of alkanes (see Section 6.1), where H_2 is generated rather than being transferred to an acceptor molecule. However, $[RhCl(CO)(PMe_3)_2]$ can be thermally activated to give $[RhCl(PMe_3)_2]$, which is a highly active transfer hydrogenation catalyst for alkanes in the presence of H_2 (Eq. (6)) [48]. 560 catalytic turnovers were observed in 25 h at 50 °C, whilst at 100 °C, 950 catalytic turnovers were achieved in less than 15 min.



(6)

In the absence of H_2, no cot was formed. It was conjectured that the two equilibria (Eqs. (7) and (8)) were in operation after initial formation of $[RhCl(PMe_3)_2]$.

$$[RhCl(PMe_3)_2] + \text{alkane} \rightleftharpoons [RhH_2Cl(PMe_3)_2] + \text{alkene} \tag{7}$$

$$[RhH_2Cl(PMe_3)_2] + CO \rightleftharpoons [RhCl(CO)(PMe_3)_2] + H_2 \tag{8}$$

$$[RhCl(PMe_3)_2] + H_2 \rightleftharpoons [RhH_2Cl(PMe_3)_2] \tag{9}$$

High pressures of H_2 will keep the equilibrium of Eq. (8) far to the left, so $[RhH_2Cl(PMe_3)_2]$ is available to hydrogenate the acceptor alkene [48]. Nonetheless, there is evidently sufficient $[RhCl(PMe_3)_2]$ present, even under the high pressures of H_2, for alkane activation to occur, so that the equilibrium constant for Eq. (9) must be very low. This is consistent with the ready production of H_2 gas from alkanes in photochemical reactions catalysed by $[RhCl(CO)(PMe_3)_2]$ (see Section 6.1). In a subsequent paper it was reported that $[RhCl(PMe_3)_2L]$ (L = P^iPr_3, PCy_3, PMe_3) or $[RhCl(PMe_3)_2]_2$ are also good, if not better, precursors for the thermal hydrogen transfer reactions from alkanes [49].

$[RhCl(PMe_3)_2]_2$ reacts with ethene to give $[RhCl(CH_2{=}CH_2)(PMe_3)_2]$. This, in a solution of cot at 170 °C under ethene (11 bar), gave 3 turnovers to cot (ethane

being the other product) in 15 h [50]. At higher pressures ethylcyclooctane and cot were produced. The system worked well up to 230 °C and 70 bar pressure, realising 32 turnovers. Under more forcing conditions, significant metallic deposition occurred. Higher turnover numbers (160 h^{-1} at 70 °C or 77 h^{-1} at 30 °C) were observed [51] at lower C_2H_4 pressures (1 bar) if the system was irradiated with visible light. $[RhCl(C_2H_4)(PMe_3)_2]$ absorbs at 416 nm, whereas $[RhCl(CO)(PMe_3)_2]$, which has been used for much of the C—H activation work, only absorbs in the ultra violet (u.v.). Labelling studies have confirmed that the reaction involves genuine hydrogen transfer and does not proceed *via* formation of free H_2 [52,53].

A potentially more useful hydrogen transfer reaction involves the use of alcohols as H_2 sources in hydroformylation reactions. Thus, $[RhH(PEt_3)_3]$ catalyses the formation of homologous alcohols from alkenes, CO (40 bar) and alcohols at 120 °C [54]. The aldehydes expected from the dehydrogenation reaction are only obtained in low yield but a variety of esters (RCO_2R') are recovered instead. For example, with ethanol and hex-1-ene all of the esters with R = Me, hexyl or 2-methylpentyl and R′ = Et, heptyl or 2-methylhexyl are observed. Yields of the alcohol products increase for $^iPrOH < EtOH < MeOH$, suggesting steric influences might be important. Complete conversion of oct-1-ene to C_9 alcohols was not observed because of a competing isomerisation reaction, but addition of hex-1-ene after a reaction of oct-1-ene was complete indicated that the catalyst retained its activity. A proposed mechanism for the transfer hydrocarbonylation is shown in Fig. 4 [54].

In related studies, it has been shown that formaldehyde can act as a source of both CO and H_2 in hydroformylation reactions (see Section 11.1) [55,56].

5. Hydrogenolysis of haloarenes

Aromatic chlorides can be dehalogenated under biphasic or phase transfer conditions using $[RhHCl_2L_2]$ ($L = PCy_3$, P^iPr_3) as catalyst [57]. Initially the catalyst loses HCl to form $[RhClL_2]$, the active species. The general reaction is shown in Eq. (10) (R is an aromatic ring, with or without other functional groups). Chlorobenzene produces benzene in 100% selectivity and 97% conversion in 24 h at 25 °C. Substituted aromatics require elevated temperatures to attain similar conversions.

$$RCl + H_2 \xrightarrow[40\%\ NaOH,\ [PhCH_2N(C_2H_5)_3]Cl]{[RhHCl_2(PCy_3)_2],\ toluene} RH + HCl \qquad (10)$$

6. Dehydrogenation

Dehydrogenation is related to transfer hydrogenation except that H_2 is evolved as a gas rather than being incorporated into another substrate. ΔG° for these reactions is positive at most accessible temperatures so that high yields are only

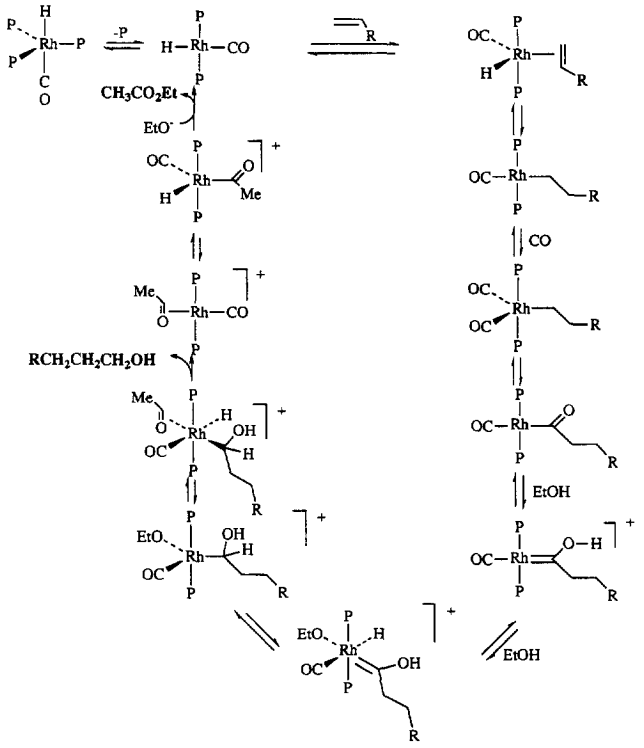


Fig. 4. Proposed mechanism for the production of heptanol from 1-hexene, CO and ethanol catalysed by $[RhHP_3]$. P = PEt_3, R = C_4H_9 [54].

obtained for photochemical reactions or for reactions in which an organic product (e.g. aldehyde) undergoes condensation or other kinds of reaction.

6.1. Dehydrogenation of alkanes

Alkanes can be photocatalytically dehydrogenated to alkenes at 55 °C in the presence of $[RhCl(CO)(PMe_3)_2]$, although for straight chain alkanes, the reaction is non-specific, giving a mixture of alkenes (see Table 1) [5,58–60].

Table 1
Selectivity of hexane dehydrogenation under various conditions

PMe_3/Rh	t/h	1-Hexene/%	2-Hexene/%	3-Hexene/%	Turnovers
2	3	7	77	15	5.4
5	3	70	24	6	4.0
5	22	51	40	9	18.7
10	3	86	12	3	0.6
10	22	67	26	7	7.2

As can be seen from Table 1, addition of free PMe_3 reduces the rate of the dehydrogenation reaction, but increases the selectivity towards hex-1-ene. At longer reaction times, the selectivity decreases, suggesting that hex-1-ene is formed first, but that the catalyst is also active for isomerisation [5]. Studies on the carbonylation of alkanes using the same system (Section 9.1) also indicate that the activation of terminal C—H bonds occurs preferentially. In addition to the presence of excess phosphine, higher temperatures and low catalyst concentration suppressed the isomerisation, suggesting that alkene coordination is a necessary prerequisite to the isomerisation reaction [61–63]. Higher rates of dehydrogenation of cyclohexane were observed (up to 200 catalytic turnovers h^{-1} at 96 °C) [64] and alcohols can also be dehydrogenated using the same system [58,65]. Even very small amounts of CO (less than 60 Torr) inhibit the dehydrogenation reaction, allowing carbonylation (see Section 9.1) to predominate [66].

The importance of the reaction (the production of high added value alkenes from cheap alkanes) has led to extensive mechanistic studies being carried out. It has been shown by flash photolysis [67] that photolysis of $[RhCl(CO)(PMe_3)_2]$ leads to $[RhCl(PMe_3)_2]$ and CO. Initially it was assumed that the subsequent reactions were all thermal so that light was only required to remove CO from the catalytic centre [5]. For this to be possible thermodynamically, it is necessary for CO to recoordinate prior to loss of H_2 or alkene. Alternatively, it has been proposed that the loss of H_2 may also be photochemically driven, although CO recoordination was still proposed (Fig. 5) [52,53].

More recently, it has been shown that the complex $[RhCl(PCy_3)_2]$, which does not contain CO, is also active for the dehydrogenation of cyclohexane [68]. No H_2 is formed in the absence of irradiation but $[RhCl(PCy_3)_2]$ reacts with cyclohexane to give $[RhH_2Cl(PCy_3)_2]$ which loses H_2 photochemically. This suggests that the mechanism operating is as shown in Fig. 6, and that the carbonyl-containing catalysts may operate by a similar mechanism but with the active catalytic species being formed by photochemical loss of CO from the catalyst precursor.

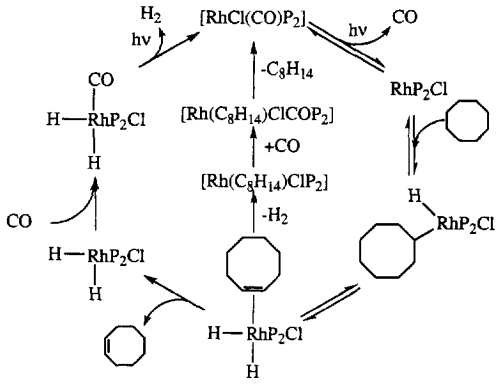


Fig. 5. Proposed mechanism for the photochemical dehydrogenation of cot catalysed by $[RhClCOP_2]$. P = PMe_3 [52,53].

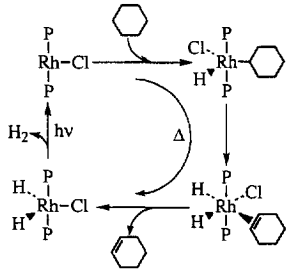
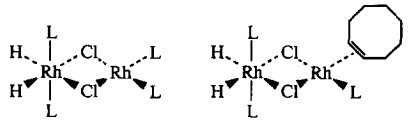
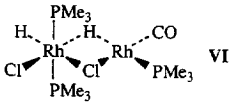


Fig. 6. Proposed mechanism for the photochemical dehydrogenation of cyclohexane catalysed by $[RhClP_2]$. P = PCy_3 [68].



IV V

NMR studies on solutions obtained from the stoichiometric addition of alkane to the catalyst $[RhCl(P^iPr_3)_2]$ indicated the presence of $[RhH_2ClL_2]$, $[RhHCl_2L_2]$ (L = P^iPr_3) and four dimers, two of which are **IV** and **V**; the other two were not fully characterised [69].

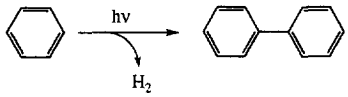


VI

Attempts to obtain more information on the hydrido species present during catalysis were carried out by monitoring the reaction of $[RhCl(CO)(PMe_3)_2]$ with *para*-hydrogen [70]. This technique is especially sensitive to metal hydrides, giving up to 200-fold improvement in signal-to-noise ratio over non-enriched hydrogen. In addition to $[RhH_2Cl(PMe_3)_3]$, a variety of other species, including **VI**, were detected.

This is an important observation, because $[RhCl(CO)(PMe_3)]$ (three-coordinate, $14e^-$, Rh^I) and $[RhH_2Cl(PMe_3)_2]$ (five-coordinate, $16e^-$, Rh^{III}), are very reactive and both are incipiently stabilised by the formation of the dimer. These results suggest that the catalytic intermediates in the dehydrogenation cycles (Figs. 5 and 6) may also be stabilised in this way, but further suggests that intermediates containing only one phosphine ligand may also be important intermediates.

Using C—H-containing substrates that are incapable of forming alkenes, coupling reactions are observed, probably *via* free radical intermediates [71]. Thus benzene gives diphenyl and H_2 (Eq. (11)).



(11)

The catalyst could also be used to dimerise other substrates; alkenes could be dimerised to dienes [72] and esters could be dimerised as in Eq. (12) [73].

$$EtCO_2Me \xrightarrow{h\nu} EtCO_2(CH_2)_3CO_2Me + MeO_2C(CH_2)_4CO_2Me \quad (12)$$

6.2. Dehydrogenation of alcohols

In addition to $[RhCl(CO)(PMe_3)_2]$ [58] (see Section 6.1), $[RhH(P^iPr_3)_3]$ and $[RhH(CO)(P^iPr_3)_2]$ are capable of producing H_2, CO and RH from primary alcohols under irradiation. If secondary alcohols are used, ketones are formed along with H_2 [47]. Similar complexes also promote the thermal or photochemical production of hydrogen from water, but the reactions are not catalytic [74].

Studies on a variety of primary and secondary alcohols have been carried out [75,76] and base is essential for the successful thermal production of H_2. The role of the base is usually to remove the aldehyde or ketone product from the reaction *via* condensation or Tishenko-type reactions, and thus alter the thermodynamics for H_2 production. In some cases, where aldehyde decarbonylation occurs, the base can also act to remove CO from the catalyst as CO_2 *via* water–gas shift-type chemistry [77]. $[Rh(bipy)_2]Cl$ and $[RuH_2(N_2)(PPh_3)_3]$ were the most active catalysts, but $[RhH(P^iPr_3)_3]$ also showed significant activity. For the ruthenium system, dihydrogen intermediates were proposed to account for the very high rates of reaction observed [76,77].

7. H—D exchange reactions

The complexes, $[RhH(P^iPr_3)_2]$ and $[Rh_2H_2(\mu\text{-}N_2)(PCy_3)_4]$, are both capable of exchanging D for H on a benzene ring using D_2O as the hydrogen source [78]. The systems are active enough to incorporate D into the methyl group of toluene, as well as the aromatic positions. Gaseous D_2 can also be used for these reactions using $[RhHCl_2L_2]$ ($L = P^iPr_3$ or PCy_3) with KOH as co-catalyst [79].

8. The WGSR and related chemistry

The WGSR involves the equilibrium shown in Eq. (13).

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (13)$$

Commercially, the reaction is carried out at high temperature, but there is considerable interest in low temperature reactions involving liquid water, since the

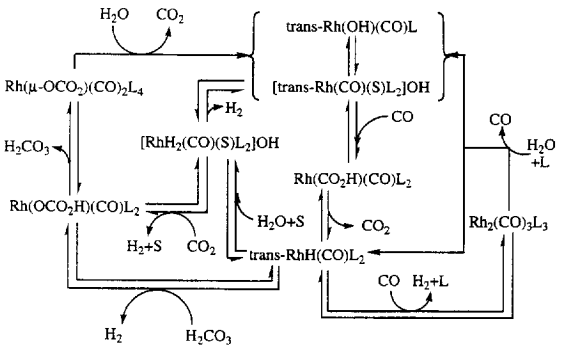
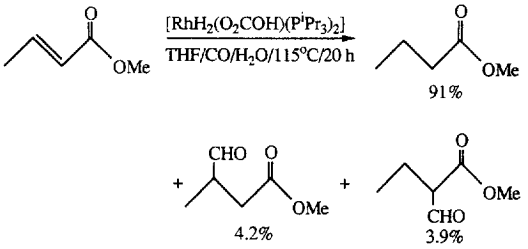


Fig. 7. Mechanism of the WGSR catalysed by *trans*-[$RhHCOP_2$]. P = P^iPr_3, S = solvent [7].

thermodynamics allow much higher conversions to H_2. Homogeneous catalysts for this reaction which give high rates under mild conditions are thus highly desirable [7,80].

Some of the most active homogeneous catalysts for the WGSR are [$RhHL_3$] (L = PEt_3 or P^iPr_3), [$Rh_2H_2(\mu\text{-}H_2)(PCy_3)_4$], *trans*-[$RhH(N_2)\{PPh(^tBu)_2\}_2$] and [$RhH(P^tBu_3)_2$]. All act as catalytic precursors for the WGSR under relatively mild conditions ($100 > T > 50\,^\circ C$). Turnover numbers of up to $35\,h^{-1}$ can be achieved at 20 bar [7]. Using model studies and isolating various intermediates using different ligands and solvents, the mechanism shown in Fig. 7 was proposed [7].

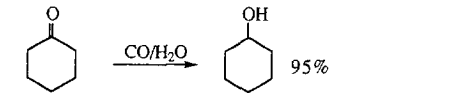
WGSR chemistry can be used in such a way that water can act as the H_2 source for a variety of reactions. Thus, alkenes, aldehydes or ketones can be hydrogenated and/or hydroformylated. A typical reaction is shown in Eq. (14) (O_2COH = bicarbonato). Here, both hydrogenation and hydroformylation of the C=C are observed [81].



(14)

The transformations shown in Eqs. (15)–(17) also occur under similar conditions [81].

$$CH_2{=}CHCN \xrightarrow{CO/H_2O} CH_3CH_2CN\ 100\% \qquad (15)$$



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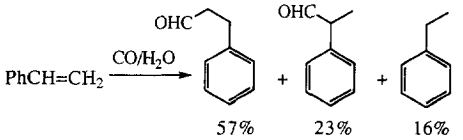
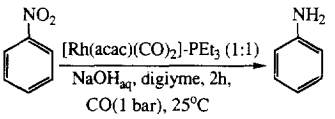


(17)

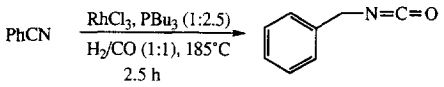
An elegant reaction uses a catalyst prepared *in situ* from $[Rh(CO)_2(acac)]$ and PEt_3 or PEt_2Ph to catalyse the reduction of nitroaromatic compounds to amines by $CO-H_2O$ (Eq. (18)) [82,83].



(18)

The catalytic turnover in the system using PEt_3 was 241, but increased to 861 at 50 °C. Substituted nitro compounds could also be reduced, e.g. *p*-chloronitrobenzene produced *p*-chloroaniline in greater than 99% selectivity [82,83].

Nitriles can be converted (greater than 90%) to isocyanates (41%) using $CO-H_2$ under WGSR conditions in the presence of $RhCl_3 \cdot 3H_2O$ and PBu_3 (Eq. (19)) [84] and CO_2 can be hydrogenated (80 bar, 40 °C) to formates in the presence of base using the same catalytic system [85].



(19)

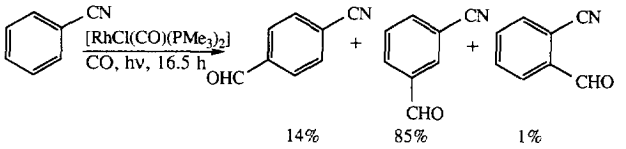
9. Carbonylation reactions

9.1. Carbonylation of C–H bonds

Probably the most exciting application of trialkylphosphine complexes of rhodium involves the catalytic carbonylation of C–H bonds to give aldehydes. This reaction occurs for a wide variety of substrates, including unactivated alkanes and arenes, and the work has been reviewed [6].

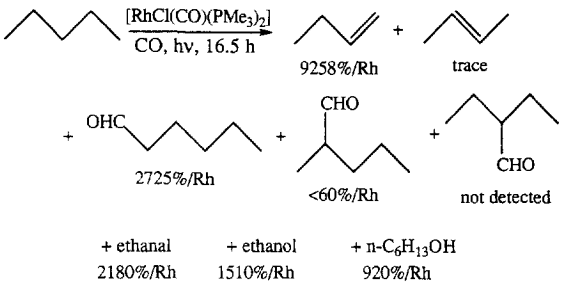
Initial studies showed that benzene could be converted into benzaldehyde (and products formed from benzaldehyde) under mild conditions (37 °C, CO (1 bar), *hν*), using $[RhCl(CO)(PMe_3)_2]$ as catalyst [86]; 47.8 turnovers had been achieved after 94 h of reaction. If PPh_3 or $P(OMe)_3$ were used, the catalyst was virtually inactive (less than 1 turnover in 16 h). Higher electron density on the metal centre favours the reaction, presumably because oxidative addition reactions are favoured by electron-rich centres.

CO inserts into the C—H bonds of substituted aromatic compounds such as nitriles, with overall conversion of 82% based on rhodium (Eq. (20)). The reaction shows some selectivity, in this case to *meta* substitution, indicating that the metal acts as an electrophile [87].



(20)

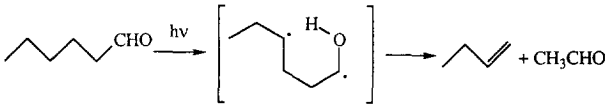
The most important of these reactions is the catalytic carbonylation of straight chain alkanes to linear aldehydes, under irradiation with u.v. light. A typical example using $[RhCl(CO)(PMe_3)_2]$ for pentane is shown in Eq. (21).



(21)

Not only is this a rare example of C—H activation in an unreactive alkane, but more importantly it was the first example where such a transformation could be rendered catalytic. It also gives the commercially desirable straight chain aldehyde [88]. Most of the products are terminal, implying that the terminal methyl groups are activated most readily. Competing formation of C_{n-1} alkenes occurs, but there is negligible isomerisation of the terminal alkenes so produced. Turnovers are reasonable (e.g. 110 in 16.5 h). It was concluded that the predominance of straight aldehyde can probably be attributed to the thermodynamic stability of the primary alkyl hydrido rhodium complex formed. This stability has been observed before in the stoichiometric activation of *n*-alkanes by $[Cp^*Rh(PMe_3)]$ ($Cp = \eta^5$-cyclopentadienyl) [89]. There is some evidence [66] that complexes containing only one PMe_3 group may be more active than $[RhCl(CO)(PMe_3)_2]$.

It is proposed that the $C_{(n-1)}$ alkenes are formed by a Norrish type II reaction (Eq. (22)). This normally occurs using u.v. light of 290 nm wavelength. Pyrex glass, in which the reactions were carried out, absorbs all light below 300 nm, so it was concluded that there was sufficient irradiation into the low energy tail of the Norrish activation band to allow the reaction to occur.



(22)

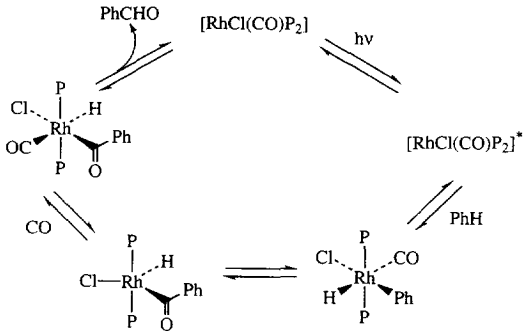


Fig. 8. Proposed mechanism for the photochemical carbonylation of benzene in the presence of $[RhCl(CO)P_2]$. P = PMe_3 [91].

Recently, detailed mechanistic studies have been carried out on the carbonylation of benzene by this system [90]. Although near u.v. irradiation does lead to photoextrusion of CO, and the product, $[RhCl(PMe_3)_2]$, is efficient at activating C—H bonds (see Section 6.1), this reaction is of little importance under the CO atmosphere of the catalytic carbonylation reaction. Instead absorption of shorter wavelength light (less than 320 nm) leads to a photoexcited state of $[RhCl(CO)(PMe_3)_2]$, which oxidatively adds benzene to give the phenyl hydrido intermediate, which decays through photochemically induced insertion of CO into the Rh—C bond. Subsequent steps are illustrated in Fig. 8. Labelling studies, which show that all four of C_6H_5CXO and C_6D_5CXO (X = H or D) are formed from mixtures of C_6H_6 and C_6D_6 have been interpreted as indicating that benzoyl chloride can reductively eliminate reversibly from $[RhHCl(COPh)CO(PMe_3)_2]$ [90]. Many of the intermediates in Fig. 8 have been isolated and characterised. Their chemistry is consistent with their being genuine intermediates in the catalytic cycle [91].

Interestingly, catalysts prepared *in situ* from $[RhCl(CO)_2]_2$ and PMe_3 appear to be up to 20 times more active than $[RhCl(CO)(PMe_3)_2]$ [92]. $[RhCl(CO)(P^iPr_3)_2]$ is not active for C—H activation [6,58] unless an aromatic ketone is added. Under these conditions, the ketone is photoexcited and removes H˙ from the alkane to give an alkyl radical, which attacks the metal centre [93].

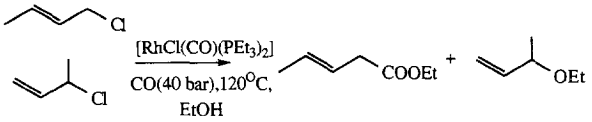
Schiff bases can be prepared from alkanes or aromatics using isocyanides in place of CO and $[RhCl(CO)(PBu_3)_2]$ [94,95] or $[RhCl(CNR)(P^iPr_3)2]$ [96,97] (not for aliphatic hydrocarbons). Thus, pentane and benzene could be converted to $MeN{=}CHC_5H_{11}$ and $MeN{=}CHC_6H_5$ respectively using MeNC.

9.2. *Carbonylation of alkyl halides*

In the presence of PBu_3 and Bu_3PO, $RhCl_3 \cdot 3H_2O$ acts as a catalyst precursor for the carbonylation of MeCl to enthanoyl chloride in 45% conversion after 2 h under CO (20 bar) in xylene [98].

$[RhX(CO)PEt_3]$ (X = OAc, Cl, Br or I) formed *in situ* from $[Rh_2(OAc)_4]$ and PEt_3 are active catalysts for the carbonylation of prop-2-enyl halides, but not EtCl

or PhCl, to butenoic acid esters if the reactions are carried out in alcoholic solvents. No additional base is required. The major competing reaction is esterification of the propenyl halides, but selectively towards the ester is highest for the prop-2-enyl chloride [99]. Interestingly, reactions carried out using either 1-chlorobut-2-ene or 3-chlorobut-1-ene give identical products (Eq. (23)), suggesting that the two ends of the allyl group become equivalent at some stage during the reaction. This could occur either because the oxidation addition occurs *via* a free-radical process or because an η^3-allyl intermediate is formed [99].



(23)

A rare example of a double carbonylation of a geminal dihalide has been reported [100] using the same catalyst system. CH_2I_2 is converted to diethylmalonate, again in ethanol in the absence of base. A bimolecular mechanism was originally proposed, but more recent studies have suggested that coordinated ketene formed from I^- loss from the proposed iodoacyl intermediate is more likely [101]. A possible mechanism is shown in Fig. 9.

Ethers can also be carbonylated in the presence of an iodide source using catalysts formed *in situ* from $RhCl_3 \cdot 3H_2O$ and PBu_3 or PPh_3 [102]. These reactions almost certainly proceed *via* a mechanism involving carbonylation of the alkyl iodide. In the example shown in Eq. (24), the substrate is completely consumed, but the products only account for 24.4% of the final product mixture if PBu_3 is omitted. The selectivity is increased to 34.5% in the presence of PBu_3. These reactions to produce levulinic acid could not be carried out using 3-butene-2-one as substrate. However, EtOH readily adds to but-3-ene-2-one to give the substrate shown in

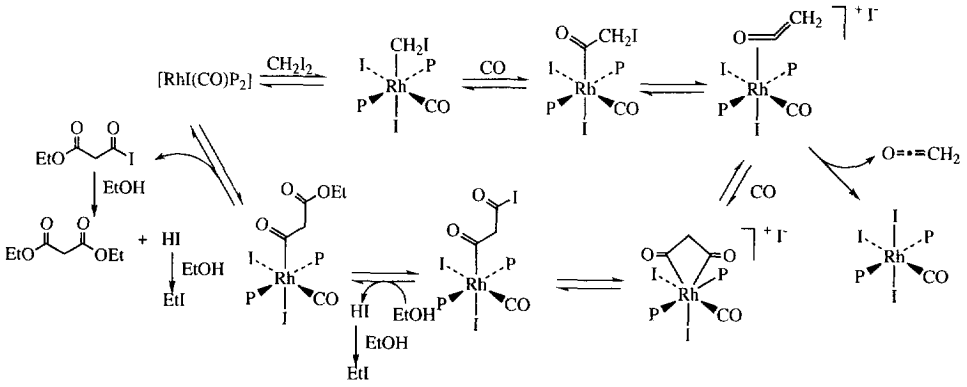
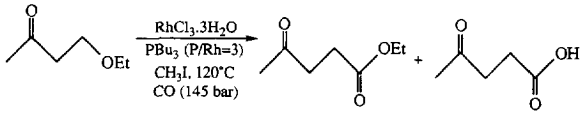


Fig. 9. Proposed mechanism for the dicarbonylation of CH_2I_2 to diethylmalonate catalysed by $[RhI(CO)P_2]$. P = PEt_3 [100,101].

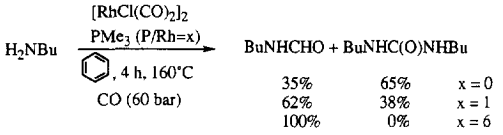
Eq. (24), thus providing a viable pathway from methylvinylketone to levulinic acid [102].



(24)

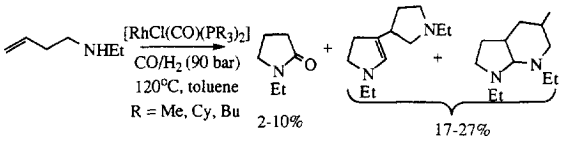
9.3. Carbonylation of amines

Primary amines can be converted into substituted formamides and ureas by using $[RhCl(CO)_2]_2$ with various phosphine ligands, including PMe_3 and $Me_2PCH_2CH_2PMe_2$, as in Eq. (25) [103].



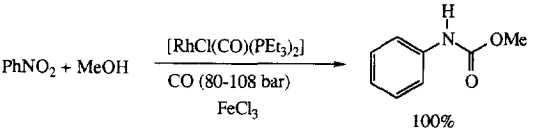
(25)

γ-lactams can be produced from the carbonylation of unsaturated amines using $[RhCl(CO)(PR_3)_2]$ (R = Me, Cy or Bu) but the reactions are non-selective (Eq. (26)) and can also be carried out using phosphine-free catalysts. $CO-H_2$ seems to give better yields than CO alone [104].



(26)

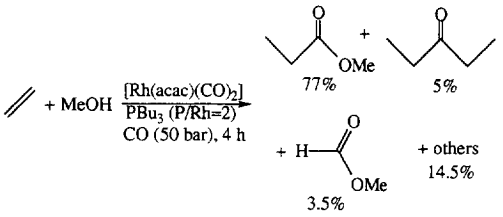
Presumably somewhat similar chemistry is involved in the reductive carbonylation of aromatic nitro compounds to urethanes (Eq. (27)). The most effective catalyst tested was $[RhCl(CO)(PEt_3)_2]$ [105].



(27)

9.4. Reppe chemistry

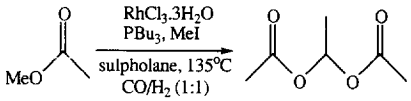
Another attractive carbonylation is the reaction of alkenes with CO in the presence of alcohols to produce carboxylic acids and/or esters (the Reppe reaction). Halide-free rhodium complexes are active for the reaction of alkenes with CO and an alcohol. A typical reaction, which proceeds with an overall conversion of 55%, is shown in Eq. (28) [106].



(28)

The production of 2-methylbutanoic acid and derivatives from 2-methylpropene or 2-methylpropan-1-ol with CO using $[RhX_2(PR_3)_2]$ (X = monovalent anion, R = alkyl, cycloalkyl, aryl) has been described [107].

Ethylidene diacetate (1,1-diacetoxyethane) can be prepared in 90% yield with a selectivity of 80% from dimethyl ether and/or methyl acetate (Eq. (29)) [108]. Ethylidene diacetate can be used as a solvent or a starting material for the production of vinyl acetate or acetic anhydride.



(29)

Esters of propanoic acid can also be formed from the reaction of ethene, but not higher alkenes, with $CO-H_2$ in the presence of hydrogen halides and $[RhCl(PPh_3)_n(PBu_3)_{3-n}]$. The activity increases as n increases [109].

10. Decarbonylation

$[RhCl(PMe_3)_2]_2$ decarbonylates aldehydes in stoichiometric quantities to give alkanes and $[RhCl(CO)(PMe_3)_2]$ [110]. Owing to the ease with which similar dicarbonyl complexes lose one CO ligand under mild conditions [111], $[RhCl(CO)(PMe_3)]_2$ was investigated. After a decarbonylation reaction using this complex, $[RhCl(CO)_2(PMe_3)]$ was isolated. This could be converted back to the dimer by purging the catalytic solution with argon, so completing the cycle. Rates were not high (3.6 turnovers h^{-1} at 100 °C, for 1-decanal) but the system was reported to be just as active after 72 h, with no sign of catalyst decomposition.

$[RhX(CO)P_2]$ (X = halide, P = phosphine) is also active for the decarbonylation (180–200 °C for 2 h) of 2-chlorocarbonylnapthalene to 2-chloronapthalene in ca. 70% yield [112].

11. Hydroformylation

Formally, hydroformylation is the addition of a hydrogen atom and a formyl group to a carbon–carbon double bond. Cobalt compounds have been known as homogeneous hydroformylation catalysts since the 1930s [9], but rhodium compounds have only been exploited since the late 1950s [1].

Normally, two aldehydes are formed from terminal alkenes. Addition of the formyl group to the terminal carbon atom gives a linear product, whereas addition of the formyl group to the internal carbon atom gives a branched chain product. It is useful to quote the selectivity of these products, when hydroformylating terminal alkenes, as a ratio in the form of linear : branched chain products or $n:i$ ratio as it is commonly termed. Linear products tend to be more commercially valuable, so a high $n:i$ ratio is often desired.

Triarylphosphine rhodium complexes [1] and trialkylphosphine cobalt complexes (which are less selective, active and stable, but give alcohols as the major products) [9] have been extensively studied, but less attention has been paid to trialkylphosphine rhodium complexes as catalysts for the hydroformylation reaction.

The main difference that has been observed using trialkylphosphine instead of triarylphosphine rhodium complexes is that alcohols rather than aldehydes can be formed under mild conditions (100–150 °C, 20–100 bar $CO-H_2$). There is also a significant effect of the solvent on the reaction products.

11.1. Hydroformylation of terminal alkenes

Using a catalyst prepared *in situ* from $RhCl_3 \cdot 3H_2O$, PBu_3 and NaOAc in ethanol [113], it was shown that after 2–3 h (195 °C, 92 bar) the major products from hex-1-ene (conversion 85%) were aldehydes (93%) but that alcohols were minor products (5.4%). After 12 h, however, the aldehyde accounted for 59.9% of the products whilst the alcohols had increased to 24.9% ($n:i$ ratios were ca. 2.5:1 in each case). These results suggest that thet alcohols are formed in a two step process *via* the aldehyde intermediates. This is logical, as it is known that similar complexes are active catalysts for aldehyde hydrogenation (see Section 3.3). Under some conditions, esters, presumably formed from Reppe-type chemistry can also be significant reaction products [114].

Extensive studies have been reported in a series of patents on the hydroformylation of hex-1-ene using rhodium-based catalysts containing trialkylphosphines, with a P : Rh ratio of less than 1.5. Complexes used include $[Rh(A)(CO)(PR_3)_2]$ (R = Bu, Et, Pr, Oc or Cy; and A is a simple carboxylate anion, e.g. OAc or acac) [115–118]. Using alkanes as solvent, the products were aldehydes (86% conversion, $n:i = 2$) together with a trace of hexane, from competing hydrogenation [115]. By changing the ratio of Rh : substrate or the solvent, the products could be altered to heptanol and 2-methylhexanol. Thus, using Rh : substrate of 1 : 100–5000 favoured the formation of alcohols, whilst ratios of 1 : 50 000–500 000 favoured aldehyde formation [115]. When alcohols were the solvent for the reaction [116], the reaction rate was enhanced at lower temperatures and homologous alcohols became the favoured products. The preferred alcoholic solvents had chain lengths greater than C_4 because acetals were formed when shorter chain alcohols were used. Detailed studies suggested that aldehydes were the primary products of these reactions, but that these were subsequently hydrogenated to alcohols.

Most of these reactions showed $n:i$ ratios of 2:1, but the hydroformylation of propene using $[RhCp(CO)(PBu_3)]$ gave only a 1:1 mixture of butanol and

2-methylpropan-1-ol [117]. A slight improvement in this ratio (greater than 1:1) was made using [Rh(acac)(CO)(PBu_3)] [118]. It is desirable to produce *n*-butanal, which has two major commercial outlets, as butanol and 2-ethylhexanol. In the industrial process, *n*:*i* ratios of 8–16:1 are routinely obtained, but only using rhodium–PPh_3 systems [119].

A comparison [120] of cobalt– and rhodium-based systems for the hydrocabonylation of octenes shows that, when using cobalt–trialkylphosphine systems, starting with a single terminal or internal octene, a mixture of all four possible isomers of C_9 aldehydes (nonanal, 2-methyloctanal, 2-ethylheptanal and 2-propylhexanal) is formed. Using rhodium–trialkylphosphine systems, however, only two isomers (nonanal and 2-methyloctanal) were formed for oct-1-ene (the *n*:*i* ratio was 1.5:1). In the same paper it was shown that but-2-ene hydroformylates to give 2-methylbutanal in the presence of excess phosphine, but isomerises rapidly without the excess phosphine present. The authors suggest that a phosphine ligand must be lost from the catalyst to allow isomerisation to occur. Therefore, excess phosphine hinders this process and increases the selectivity of the reaction.

A variety of other catalysts have been reported in the patent literature. These include Rh—C (5%) in the presence of PBu_3 [121,122]; [$Rh(PBu_3)_3]_2$ [123]; [$RhH(CO)(P^iOc)_3$] (Oc = octyl) [124]; [$RhCl(CO)(PR_3)_2$] (R = Bu, Oc or $C_{16}H_{33}$) [125] and a system involving a catalyst prepared *in situ* from a 1,5-cyclooctadiene imidazole rhodium trimer in the presence of PEt_3 [126]. Most of these complexes show reasonable activity at temperatures at or below 100 °C, with aldehydes as the major product and *n*:*i* ratios of about 2.5:1.

A study was carried out on 1,3-butadiene using Rh_2O_3 modified with various phosphines (PMe_3, PEt_3, POc_3, P^iPr_3, P^tBu_3 and $P(c\text{-}C_3H_5)_3$). The reaction conditions were fairly severe (200 bar; $CO—H_2$ 1:1, 130 °C), but selectivities were high in the monoaldehyde (*n*:*i* > 10:1). In the dialdehyde, the ratio *n,n*:*n,i* tended to be of the order of 1:2–5), the yields are between 43–77%. It was found that P^iPr_3 gave a slightly faster rate and better selectivity than PPh_3 [127].

Recently, detailed studies [8,26,54,128] of the hydrocarbonylation of a variety of alkenes using [$RhH(PEt_3)_3$] as catalyst precursor have been reported. In toluene the major products are heptanal and 2-methylhexanal. In tetrahydrafuran (thf), aldehydes are the products after 2 h of reaction, but alcohols are selectively formed after longer reaction times (16 h). Using alcoholic solvents, however, heptanol and 2-methylhexanol are the only products even after only 2 h of reaction; labelling studies suggest that they are the primary products. Thus, using D_2 in EtOH the heptanol formed is almost exclusively $C_4H_9CHDCH_2CD_2OH/D$, whilst the hydrogenation of heptanal under identical conditions produces a mixture of $C_6H_{13}CHDOH/D$ and $C_6H_{13}CH_2OH/D$ (see Section 3.3). A mechanism has been proposed in which the high electron density on the metal as a result of the electron donating phosphines renders the oxygen atom of the metal-bound acyl specifies sufficiently negatively charged for it to be protonated by the alcoholic solvent to give a hydroxycarbene intermediate (Fig. 10). This proposal is supported by the detection by NMR of an analagous hydroxycarbene complex, $[Rh(=C(H)OMe)CO(PEt_3)_2]^+$ synthesised as shown in Fig. 11. The carbene

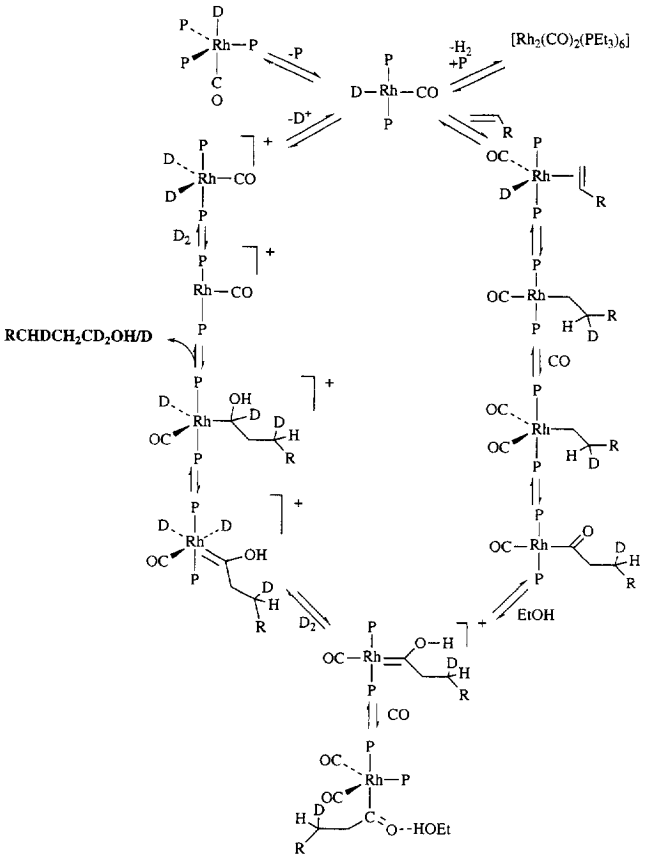


Fig. 10. Proposed mechanism for the hydrocarbonylation of alkenes using D_2 catalysed by $[RhHP_3]$, showing the labelling pattern of the linear alcohol product. P = PEt_3; R = C_4H_9 [8,26].

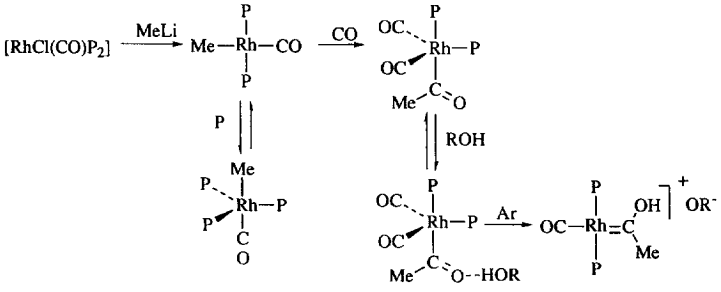
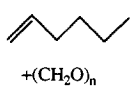


Fig. 11. Synthetic procedure for the synthesis of an analogue of the hydroxycarbene intermediate proposed in Fig. 10. P = PEt_3; R = alkyl [8].

C atom resonates at δ 304 ppm. The activity of this catalytic system is very high with turnover numbers up to 54000 h^{-1} for C_2H_4 at 120 °C and 40 bar $CO-H_2$, but $n:i$ ratios were only of the order of 2–3:1. A study of the effect of different phosphines shows that alcohols are only produced using tris(primaryalkyl)phosphines, whereas acetals are the major products if PPh_3 or no phosphine is present, and P^iPr_3 promotes the formation of aldehydes. Catalysts for these studies were prepared *in situ* from $[Rh_2(OAc)_4]$ and the phosphine [8].

Gaseous H_2 and CO can be replaced by paraformaldehyde in hydroformylation reactions using trialkylphosphine complexes such as $[RhH_2(O_2COH)(P^iPr_3)_2]$ as catalyst precursors (Eq. (29)) [55].



$C_6H_{13}CHO + C_6H_{13}CH_2OH$ (67%) (4%)

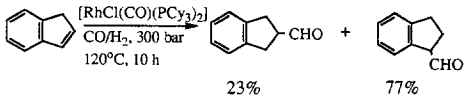
$+C_6H_{13}CO_2CH_3 + C_6H_{14}$ (13%) (3%) (30)

The overall conversion using P^iPr_3 was 100%. However, when using PPh_3-derived catalysts the yield was virtually 0%. A rise in temperature to 150 °C caused an increase in formation of alcohols and esters, at the expense of aldehydes. When using $C_6H_{13}CHO$ as substrate, instead of hex-1-ene, then alcohols and esters were again formed. This suggests that at least one pathway to making alcohols and esters involves the disproportionation of the aldehyde initially formed [55]. Other complexes, such as $[RhH(N_2)L_2]$ ($L = P^tBu_3$, P^iPr_3). $[Rh_2H_2(\mu\text{-}N_2)(PCy_3)_4]$, $[RhHL_3]$ ($L = P^iPr_3$, PEt_3), are also active catalysts for hydroformylation using paraformaldehyde [56].

11.2. Hydroformylation of hindered and internal alkenes

2-butene can be hydroformylated selectively to 2-methylbutanal using carbonylhydridophosphinerhodium compounds. The best phosphines contained the same three C_{3-10}(cyclo)alkyl groups and it was stipulated that the cone angle should be 159–171°; 88% conversion and 98% selectivity were achieved, 2-methylbutanal being produced in 32:1 ratio over other products [129]. With unsymmetrical internal alkenes, two products are observed. There is no evidence for formation of the linear product as a result of isomerisation of the alkene prior to hydroformylation. Thus, hydroformylation of hex-2-ene in ethanol using $[RhH(PEt_3)_3]$ as catalyst precursor gives a mixture of 2-methylhexanol and 2-ethylpentanol, but no heptanol [8].

Using the catalyst precursor $[Rh(OAc)(cod)]_2$ modified with P^tBu_3 or PCy_3, it was possible to hydroformylate cyclohexene under relatively mild conditions (10–20 bar, 70–90 °C) [130]. Owing to the symmetry of the substrate, only one product, cyclohexanal, was formed. Rates were similar to that obtained with PPh_3, but sluggish compared with those with bulky triarylphosphines. $[RhCl(CO)(PCy_3)_2]$ has also been used for the hydroformylation of indene in 93% yield, as in Eq. (31) [131].



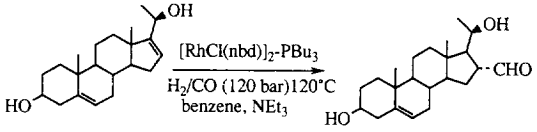
(31)

Trialkylphosphine rhodium complexes are the preferred catalysts for the hydroformylation of 2-substituted alkenes [130,132]. For example, using $[Rh(OAc)(cod)]_2$ and 2-methylhex-1-ene as substrate, only the terminal C atom was functionalised because, for steric reasons, anti-Markownikoff addition of the Rh—H bond across the double bond to give the primary alkyl intermediate is very much preferred over Markownikoff addition to give the tertiary alkyl rhodium complex [130]. With $[Rh(acac)(CO)_2]$ and highly hindered tricycloalkylphosphines (ring size 3–14 C atoms), aldehydes and alcohols could be made in ca. 21% yield. This was compared with 0.3% when using PPh_3 [132].

The first step of a four step procedure to convert 2-methylbutene to 2-hydroxymethyl-2,3-dimethylpentan-1-ol [133] (a useful synthon in the pharmaceutical industry for the production of carbamates, which find applications as tranquilizers and anti-hypertensives), involved the hydroformylation of 2-methylbut-1-ene using [Rh(2-ethylhexanoate)$_3$] in the presence of PBu_3. The product was 2-methylpentanal (100% conversion, 93% selectivity), but forcing conditions (250 bar, 130 °C) were employed.

High boiling point substrates, such as unsaturated fatty acids (16 to 18 carbon atoms), have been hydroformylated using a soluble rhodium compound such as $[Rh(acac)(CO)_2]$ in the presence of trialkylphosphines [134]. The phosphines used were unusual in the fact that the alkyl groups on each phosphine contained a total of 24 or more carbon atoms (e.g. POc_3, $P(C_{12}H_{25})_3$ etc.). The hydroformylation conversion was high (greater than 95%), with greater than 95% selectivity towards aldehydes. In comparison, the conversion dropped to 60% when PEt_3 was used, and 5% using PPh_3 [134].

Another example of the more specialized use of the trialkylphosphine–rhodium systems is the hydroformylation of a steroid skeleton (Eq. (32)), which proceeds in 88% yield with greater than 99% selectivity [135].



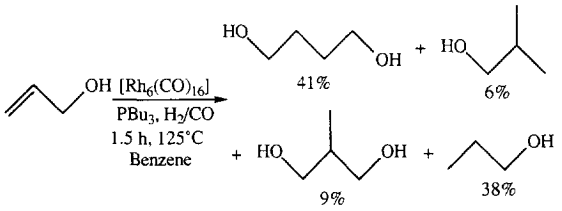
(32)

11.3. Hydroformylation of oxygen-containing alkenes

1,4-butanediol is an important medium volume chemical used in the synthesis of polyesters and, by dehydration, in thf synthesis. Many studies on its formation by hydroformylation of prop-2-en-1-ol have been carried out. Indeed, the commercial Kuraray process involves the use of $[RhH(CO)(PPh_3)]$ to catalyse the selective formation of 4-hydroxybutanal, which is subsequently hydrogenated to 1,4-butanediol [136].

Since trialkylphosphine rhodium complexes can catalyse the *direct* formation of alcohols (see Section 11.1), it is attractive for them to be used in the synthesis of butane-1,4-diol since this will allow the reaction to be carried out in one pot and eliminate the intermediate 4-hydroxybutanal which may be susceptible to aldol condensation and internal acetal formation. The presence of the alcohol function in the substrate means that alcohols rather than aldehydes may be the products even in aromatic solvents.

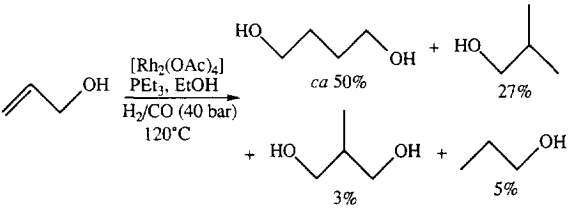
Patents cover the use of rhodium carbonyl complexes with a wide variety of phosphines for the hydrocarbonylation of prop-2-en-1-ol [137,138]. The phosphines that gave the best results were trialkylphosphines. Typical results are shown in Eq. (33).



(33)

Substituted allyl alcohols (e.g. $HOCH_2CH{=}CMe_2$) were only hydroformylated in low yield, but without any isomerisation [138]. Hydroxyaldehydes can also be formed in high yield using related catalysts such as $[RhH(CO)(PR_3)_3]$ (R = Bu or Cy) [139,140]. The *n*:*i* ratios in these reactions can be as high as 28:1, but in these cases, the overall yields are disappointing. Higher boiling point products can account for as much as half of the product stream [140].

Recently, detailed studies have been reported on the hydrocarbonylation of prop-2-en-1-ol using $[Rh_2(OAc)_4]$ and PEt_3 as catalyst precursors [27,28]. In ethanol at 120 °C and with $H_2{-}CO$ (40 bar), the major products are as shown in Eq. (34).



(34)

This product distribution is of importance since the major branched chain product is not 2-methylpropan-1,3-diol but rather 2-methylpropan-1-ol. The latter can be much more easily separated from 1,4-butanediol since their boiling points are separated by more than 120 °C. Studies under a variety of different conditions show that the primary reaction products are 1,4-butanediol, produced by a mechanism analogous to that shown in Fig. 8, and 2-methylpropanal, which is subsequently hydrogenated to 2-methylpropan-1-ol. Labelling (using $CO{-}D_2$ in EtOH, $CO{-}H_2$ in EtOD and $CO{-}D_2$ in EtOD) has been used to study the mechanism of the formation of 2-methylpropan-1-ol and, although complex mixtures of multiply labelled products

are formed, which require special $^{13}C\{^{1}H, ^{2}D\}$ NMR techniques for full quantitative analysis [141], the mechanism proposed in Fig. 12 is fully consistent with the observed results. Changes in the H/D content of the solvent OH/D make quantitative analysis difficult, but it was possible to calculate a primary kinetic isotope effect of 4 for the isomerisation of the vinyl alcohol to 2-methylpropanal. This is similar to values that have been obtained for related isomerisations using acid, base [142] or metal complex catalysts [143].

1,4-Butanediol can also be obtained (after hydrogenation) from the hydroformylation of cyclic acetals of $CH_2{=}CHCHO$ (with 1,3-diols) using Co or Rh trialkylphos-

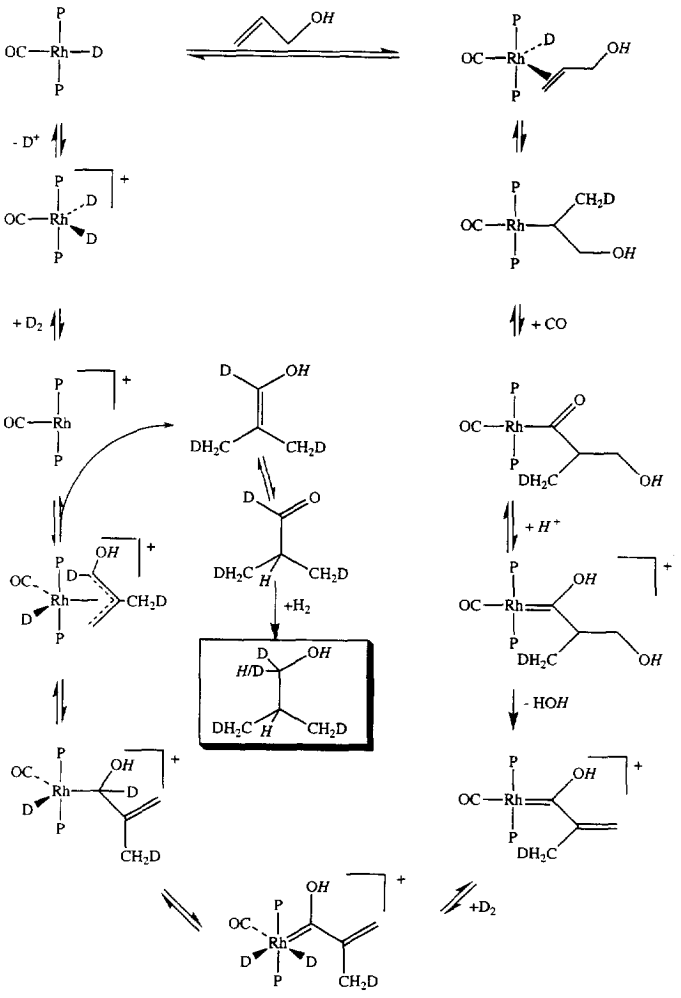
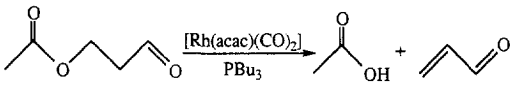


Fig. 12. Proposed mechanism for the production of 2-methylpropan-1-ol during hydrocarbonylation of 2-propen-1-ol catalysed by $[RhHP_3]$. Atoms labelled D are derived from the gas phase, whilst atoms labelled *H* are derived from the O*H* of the solution. P = PEt_3 [27,28].

phine complexes [144], or in up to 69% yield from prop-2-en-1-ol using $[Rh(acac)(CO)_2]$, PR_3 (R = Me, Et, Bu, Oc) and a carbonitrile solvent of the general formula $R'CH_2CH_2CH_2CN$ (R' = H or a hydrocarbyl group) [145].

Propenyl ethers ($ROCH_2CH{=}CH_2$, R = Ph, Et or propenyl) can be hydroformylated using $[Rh_2(OAc)_4]-PEt_3$ in ethanol [28]. The major products are 4-hydroxybutyl ethers, 2-methylpropan-1-ol and the alcohol (ROH), although for dipropenylether, 1,4-butanediol is also formed, presumably from the prop-2-en-1-ol released. It is assumed that the products are formed in an analogous fashion to those from prop-2-en-1-ol in the same system (Figs. 10 and 12) except that the alcohol rather than water is lost from the hydroxycarbene intermediate analogous to that shown in Fig. 12. Small amounts of butanol are also obtained from this reaction. Using 3-butene-1-ol as substrate, the same catalyst system produces largely the diols, 1,5-pentanediol and 2-methylbutanediol. In this case there is no driving force of conjugation assisting any dehydration reaction [28].

Vinyl ethers give 1:1 ratios of 2- and 3-alkoxypropanals on hydroformylation using rhodium carbonyls in the presence of PBu_3 [146] whilst vinyl esters also give the expected linear and branched products [147]. Interestingly, the branched chain products predominate, as the rhodium trialkyl phosphine complexes are especially active for the degradation of the straight chain product by the process shown in Eq. (35) [147].



(35)

A process for the hydroformylation of 2-methylbut-1-en-4-ol used a catalyst prepared *in situ* from a rhodium complex and various phosphines, including PBu_3 and PCy_3. Yields of 2-hydroxy-4-methyltetrahydropyran were 85–90%. The product was then reduced using a suitable hydrogenation catalyst to give 3-methylpentane-1,5-diol, which has been used in the production of polyurethanes [148].

Epoxides, which are similar to vinyl compounds, have been hydroformylated to 1,3-diols. For example, ethene oxide is converted to 1,3-propanediol in 28% yield using $[Rh(acac)(CO)_2]-PCy_3$ at 120 °C and 100 bar in the presence of HI and hydroquinone [149].

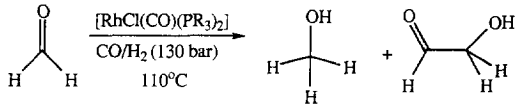
Using $[Rh_6(CO)_{16}]$ and PBu_3 or PCy_3, vinyl chloride can be converted to 2-chloropropanal in 12–14% yield and 81.5–83.1% selectivity (the best phosphine employed was triphenylphosphine, giving 29.5% yield and 88.4% selectivity) [150].

12. Production of 1,2-ethanediol from $CO-H_2$ with or without formaldehyde

There has been considerable interest in discovering new routes to 1,2-ethanediol, which is currently produced from ethene, an oil-based feedstock, especially by the homogeneous hydrogenation of carbon monoxide or hydroformylation of formaldehyde. Methanol is often a major by-product in these reactions, 1,2-ethanediol is

useful as a starting material for polyester fibres and organic solvents, or as a low volatility antifreezing agent.

The first reported synthesis of 1,2-ethanediol using rhodium–phosphine systems was *via* the hydroformylation of formaldehyde. 2-hydroxyethanal was the final product (Eq. (36)), which could easily be hydrogenated to 1,2-ethanediol [151].



R = Cy	2.5%	9%
R = Bu	4.8%	3.7%
R = Ph	2.3%	39.8%

(36)

1,2-ethanediol and methanol could be produced directly from CO and H_2 (430 bar, 220 °C) using Rh–trialkylphosphine systems and an N-containing base such as *N*-methyl pyrrolidinone [152]. Rates of production of 1,2-ethanediol as high as 30 mol $(g\ Rh)^{-1}\ h^{-1}$ were observed, but the selectivity to the diol was generally less than 50%, the major product being methanol. It was found that bulky trialkylphosphines, such as P^iPr_3, were the most useful ligands in 1,2-ethanediol formation. Complexes containing arylphosphines, alkyl or aryl phosphites and small cone angled alkyl phosphines all decomposed to form inactive clusters, $[Rh_9P(CO)_{21}]^{2-}$ being one of the major species identified.

A range of supporting ligands/co-catalysts can be used. For instance N-oxides, phosphine oxides, 1,4-diazabutadiene derivatives and silicon compounds are all active. Even cationic rhodium complexes can be used [153]. One rhodium compound contained a phenoxo or substituted phenoxo ligand incorporated in the active catalyst [154]. High boiling point solvents with amines can give high conversions and selectivity to 1,2-enthanediol. Thus, $[Rh(CO)(p\text{-}MeOC_6H_4O)\{P(Bu)^tBu_2\}_2]$ (2 mmol) in tetraglyme (30 cm^3) and *N*-octylpyrrolidine (20 cm^3) at 215 °C for 10 min would give 1,2-ethanediol (56.9 mmol) and methanol (9.5 mmol) from $H_2{-}CO$. The low boiling point products could be separated by distillation and the system would run again without any loss in activity [155].

A range of mechanistic studies has been carried out on this important reaction. From high pressure infra red (i.r.) studies, it was proposed that [HRh(CO)$_3$(phosphine)] was the main catalytically active species [156]. Subsequently, yields were increased slightly using carboxylate ligands. Thus compounds such as $[Rh(PhCOO)(CO)(PR_3)_2]$ (R = ^{i}Pr or Cy) were found to be quite effective [157]. A strange effect was discovered [158] whilst varying the pressure of the system. When the pressure was doubled from 500 to 1000 bar the activity for P^iPr_3 and PCy_3 systems doubled. For the system containing PBu_3, the enhancement was ca. 20-fold. This was investigated using high pressure i.r., and it was found that in the PBu_3 system rhodium carbonyl clusters, $[Rh_9P(CO)_{21}]^{2-}$ and $[Rh_6(CO)_{15}]^{2-}$, were the predominant species at 500 bar. However, at 1000 bar, two complexes, thought to be $[RhH(CO)_4]$ and $[RhH(CO)_3(PBu_3)]$, were the main species present. On cooling down the catalytic mixtures (originating from $[Rh(CO)_2(acac)]$ and

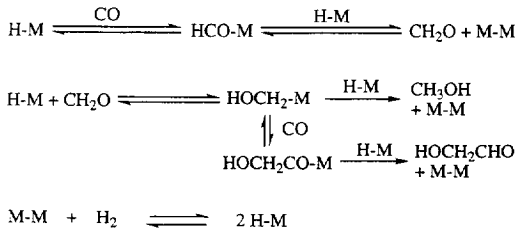


Fig. 13. Proposed mechanism for the production of methanol and/or 1,2-ethanediol from CO and H_2 catalysed by $[RhCl(CO)(PR_3)_2]$. M = $[Rh(CO)_3PR_3]$, R = Bu, ^{i}Pr, Cy or Ph [161].

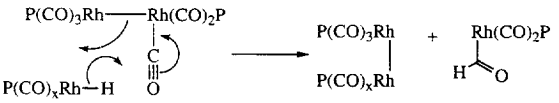


Fig. 14. Possible mechanism for the formation of the crucial formyl intermediate during the catalytic hydrogenation of CO catalysed by $[RhCl(CO)P_2]$. P = PBu_3, P^iPr_3, PCy_3 or PPh_3.

P, P = P^iPr_3 or P[c-C_5H_9]$_3$), a strong i.r. absorption at 1959–1960 cm^{-1} was observed. The rhodium complexes formed were isolated and found to be $[Rh(CO)_3P]_2$. These complexes could be used as the starting catalysts and the activity was unchanged. An equilibrium was thought to exist at ambient temperatures between $[Rh(CO)_3P]_2$ and $[RhH(CO)_xP]$ in the catalytic system [159]. A Rh:phosphine ratio of 1:1 was the best for bulky phosphines [160]. This also suggests that the active species contains only one PR_3 group.

A mechanism which accounts for the catalytic activity of both $[Rh(CO)_3P]_2$ and $[RhH(CO)_xP]$ in the CO hydrogenation reaction (Fig. 13) has been proposed [161].

Formaldehyde formation is the rate determining step in Fig. 13, and the reductive eliminations all result in binuclear products, from which the mononuclear species can be regenerated by reaction with hydrogen. Phosphine ligands are proposed to facilitate the insertion of CO into the Rh—H bond in the formation of the crucial formyl intermediate [157]. However, this insertion reaction has only been observed in very unusual systems [162,163], and studies on ruthenium-based systems have suggested that intermolecular H^- transfer from one metal centre to CO bound in another complex is a more likely process for the formation of the formyl intermediate [164–166]. Since the hydride is more hydridic in complexes containing the strongly electron donating trialkylphosphines, the promoting effect of the phosphine may involve increasing the rate of intermolecular hydride transfer. The observation of the two species, $[Rh(CO)_3PR_3]_2$ and $[HRh(CO)_xPR_3]$ in the catalytic system makes it tempting to speculate that the formyl intermediate might be formed as in Fig. 14.

13. Addition of aldehydes to substrates

The addition of formaldehyde across double bonds has already been discussed in Section 11.1. In a related reaction, five-membered cyclic ketones can be prepared

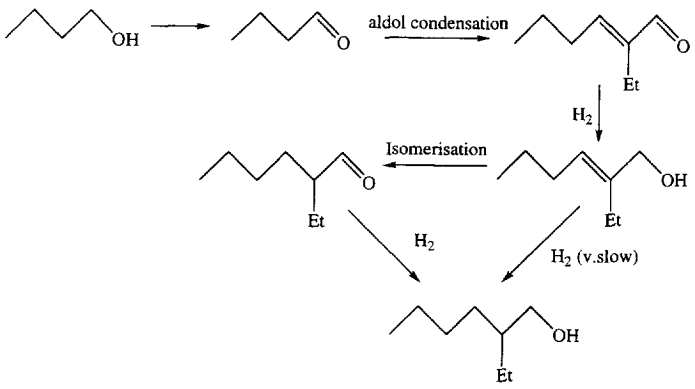
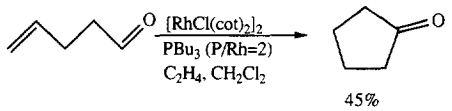


Fig. 15. Organic intermediates in the formation of 2-ethylhexanol from butanol *via* the Guerbet reaction [168,169].

from unsaturated aldehydes by an intramolecular cyclisation reaction (Eq. (37)) [167].



(37)

Tri-*p*-tolyl, tri-*p*-methoxyphenyl and tris(*p*-dimethylaminophenyl)phosphine were the best ligands giving greater than 90% yield. PEt_3 and PCy_3 gave yields of between 30 and 70%. The reaction was tolerant of other functional groups in the reactant aldehyde, but only five-membered rings could be synthesised.

The Guerbet reaction, which involves the dimerisation of alcohols, can be catalysed by rhodium–trialkylphosphine systems [168,169]. This reaction is of particular importance since it allows the formation of, e.g. the important plasticiser precursor, 2-ethylhexanol in one step from butanol, whilst the usual procedure involves the aldol condensation of butanal followed by hydrogenation. Either butanal or butanol are available from hydroformylation reactions. The transformation was performed over $[Rh(CO)_2Cl]_2-8PEt_3$ or $RhCl_3 \cdot 3H_2O-4PBu_3$ in yields in the range of 85–90%. The mechanism is shown in Fig. 15.

C—H bonds activated by a nitro group can be added across the C—O bond of aldehydes in a reaction similar to catalysed aldol condensation (Eq. (38)) [170].

$$MeNO_2 + MeCHO \xrightarrow[23\,^{\circ}C,\ 0.5\,h]{[RhCl(PMe_3)_3]} MeCH(OH)CH_2NO_2 \quad >90\% \qquad (38)$$

14. Other addition reactions

14.1. Hydrosilylation

Generally, it has been found that rhodium trialkylphosphine complexes are inferior to those containing PPh_3 [171,172] for the hydrosilylation of alkenes. However,

tricyclohexylphosphine is one of the most active promoters for the hydrosilation of terminal alkenes [173,174], dienes [174] or alkynes [174], additionally it shows greater selectivity towards addition of the silicon atom to the terminal C atom of hex-1-ene or oct-1-ene. With dienes, or alkynes, selective (60–70%) formation of monoene silanes is observed. The reaction of hex-1-yne was investigated in some detail and sampled at periods during the 8 h reaction. The $Z:E$ ratio was always close to 1:1.

Since most catalysts give a product that is predominantly E, due to *cis* addition of the hydrogen atom and silyl group (mixtures of Z and E products from rhodium catalysts have precedents in the literature) [175,176], the authors propose two possible explanations. Either addition is not stereospecific, or slow stereospecific addition takes place followed by rapid isomerisation. Other rhodium catalysts, however, show only slow Z/E isomerisation for alkenes [175,176]. Cyclic or acyclic ketones can also be hydrosilated with greater than 70% selectivity using catalysts based on PCy_3 [174] or PBu_3 [177].

3-aminoprop-1-ene has also been used as a substrate for hydrosilation reactions at 120°C in the presence of $[RhCl(cod)]_2$ and PEt_3 [178,179]. Yields are of the order of 75% and the selectivity towards the terminal product is higher using PEt_3 (55:1) than using PPh_3 (24:1).

Under near u.v. irradiation, hydrosilylation occurred between $[(CH_3)_2SiH]_2O$ and $[H_2C{=}CHSi(CH_3)_2]O$, when exposed to air [180]. The reaction used a $Rh(I){-}PBu_3$-based process, rhodium being introduced as $RhCl_3 \cdot 3H_2O$ or $[RhCl(CO)_2]_2$. The reaction was aided by the prsence of air or an oxidising agent, which presumably allows the formation of the phosphine oxide, which might then weakly stabilise the complex, but readily create a vacant site.

In the presence of $[RhCl(CO)(PMe_3)_2]$, toluene can be silylated by $Me_3SiSiMe_3$ on the ring or the methyl C atoms, but with little selectivity (Eq. (39)) [181].

$$+ Me_3SiSiMe_3 \xrightarrow[[RhCl(CO)(PMe_3)_2]]{h\nu} MeC_6H_4(2\text{-},3\text{-},4\text{-})SiMe_3 + PhCH_2SiMe_3 \qquad (39)$$

Rhodium-based catalysts have been employed to react secondary alcohols or ketones with silanes [182]. The aim of the work was to make trifunctional silanes with different substituents to induce chirality. The first step of the method was to use a rhodium catalyst to obtain monosubstitution on the silane (Eq. (40)), R = α-naphthyl).

$$\underset{1}{RSiH_3} + \underset{1}{{}^iPrOH} \xrightarrow[C_6H_6]{[Rh(Cl(PCy_3)_2]} \underset{36\%}{RSi(O^iPr)H_2} + \underset{64\%}{RSi(O^iPr)_2H} + H_2 \qquad (40)$$

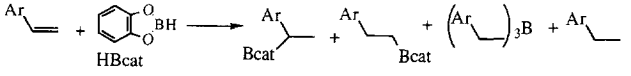
A chiral silane was produced, but it failed to give any significant chirality in the products obtained from hydrosilation reactions attempted with it.

$[RhCl(CO)(PEt_3)_2]$ has been used to form aldehydes and ketones from benzoyl-chlorides in the presence of triethylsilane [183]. Yields of 27% ketone (e.g. benzophenone from benzoyl chloride) and 4% aldehyde were produced.

14.2. Hydroboration of alkenes

Although water can be added across the double bonds of alkenes in acid-catalysed reactions, the products are invariably formed by Markownikoff addition, so that secondary alcohols, rather than the more commercially valuable primary alcohols, are produced. As yet, there have been no reproducible examples of the use of metal-based catalysts for the hydration of alkenes, so that there is no simple method for the direct production of terminal alcohols from the addition of water across the double bond. One indirect method that has received extensive study is the hydroboration of alkenes followed by oxidation of the borane so formed using aqueous hydrogen peroxide. Often, the borane used in the hydroboration reaction is catecholborane and both straight chain and branched chain products can be produced. Small amounts of hydrogenation of the alkene sometimes occur, and the metal-based catalysts sometimes act to degrade the catacholborane to give first BH_3 and then trialkylboranes obtained from the addition of each of the B—H bonds of BH_3 across the double bond (Eq. (41)). Some of the most effective hydroboration catalysts are triphenylphosphine complexes of rhodium [1c] but rhodium trialkylphosphine complexes have been investigated [184,195].

$[RhCl(N_2)(P^iPr_3)_2]$ is one of the most selective and active catalysts for the hydroboration of 2-phenylpropene, giving a linear : branched ratio of 90 : 1, with 10% being hydrogenated to 2-phenylpropane [184]. A catalyst prepared *in situ* from $[RhCl(cot)_2]_2$ and PPh_3 gave 98% of the desired straight chain product and only 2% hydrogenation. No branched chain product was observed. More extensive studies using 4-methoxystyrene as substrate have shown [185] that $[RhX(N_2)(PR_3)_n]$ (R = ^{i}Pr, X = H or Cl, $n = 2$; R = Me, X = Cl, $n = 3$) or $[RhH(PMe_3)_4]$, which produces $[RhH_2(PMe_3)_4][B(cat)_2]$ (cat = catecholate) under the reaction conditions, are all active catalysts. The hydrides give substantial amounts of products derived from degradation of the catechol borane and some hydrogenation products, but the less basic chloro complexes give little or none of these products. The branched chain products may arise *via* intermediates involving η^3-benzyl interactions, but the more bulky P^iPr_3 ligand reduces the importance of these products (see Eq. (41)).



$[RhH(N_2)(P^iPr_3)_2]$	45%	45%	5%	5%
$[RhH(PMe_3)_4]$	38%	38%	13%	4%
$[RhCl(N_2)(P^iPr_3)_2]$	5%	95%		
$[RhCl(N_2)(PMe_3)_2]$	45%	55%		

Ar = 4-MeOC$_6$H$_4$ (41)

14.3. Hydroamination of alkenes

There are very few catalysts that promote the catalytic addition of amines to olefinic double bonds. A system generated *in situ* from $[RhCl(PMe_3)_2]_2$ and LiNHPh gives [186] mixtures of hydroamination ($RCH_2CHNHPh$, linear, RCH(Me)NHPh, branched) and oxidative hydroamination (RC(Me)=NPh) products from alkenes

and aniline. For R = Ph, 21 catalytic turnovers were observed with the oxidative hydroamination product being obtained in 65% yield. The linear:branched ratio for the hydroamination products was 1:6, although there is some evidence that the linear product arises from an uncatalysed reaction. For R = Bu, only branched products were observed, but 85% of the product was the oxidative hydroamination product [186]. Interestingly, when norbornene is used as the substrate, the slow catalytic reaction (25 turnovers, 70 °C, 12 days) only gives small amounts (33%) of the expected hydroamination product. The main product is formed by addition of an *ortho*-C—H bond of the phenyl ring of aniline across the double bond. Using diphenylamine in place of aniline, the product from C—H activation is exclusively observed [187].

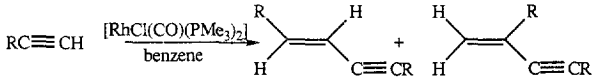
14.4. Kharasch reactions

The addition of $CBrCl_3$ to double bonds generally occurs *via* a free radical mechanism. However, it has been shown [188] that a more classical oxidative addition/insertion pathway is followed if $[RhCl(CO)(PMe_3)_2]$ is used as catalyst. $[RhBr(CCl_3)Cl(CO)(PMe_3)_2]$ has been isolated and shown to be as active as $[RhCl(CO)(PMe_3)_2]$.

15. Oligomerisation or telomerisation reactions

15.1. Dimerisation

In the absence of light $[RhCl(CO)(PMe_3)_2]$ catalyses the dimerisation of alkynes as shown in Eq. (42) [189–192].

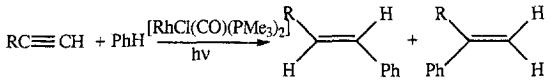


R =	Pr	37%	63%
	^{t}Bu	100%	0%
	Ph	0%	100%
	$MeOC_6H_4$	0%	100%
$Me_2C{=}CH(CH_2)_2CMe{=}CH(CH_2)_2CMe(OH)$		100%	0%

(42)

The effect of phosphine ligand on the linear:branched ratio in the dimerisation reaction has been explained [193]. Thus, electron donating ligands, such as PBu_3, promote the formation of linear dimers unless they are very bulky (e.g. PCy_3), in which case the branched product is favoured as a result of steric hindrance.

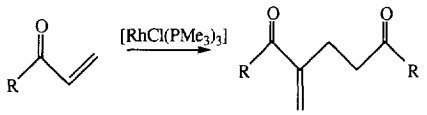
When this reaction is carried out under illumination with u.v. light, the C—H bonds of benzene are activated preferentially and substituted styrenes are formed (Eq.(43)) [190].



R =		
Pr	68%	14%
^{t}Bu	48%	10%
Ph	0%	90%
$MeOC_6H_4$	0%	95%

(43)

$[RhCl(PMe_3)_3]$ also catalyses the dimerisation of methylvinylketone (Eq. (44)) [194,195].



(44)

The catalytic addition of carbenes, generated in situ from diazoalkanes, to alkenes gives longer chain alkenes rather than cyclopropanes, which might have been expected (Eq. (45)) [196].

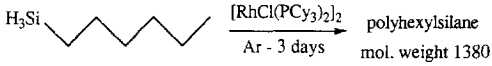
$$N{=}N{=}CRR' + CH_2{=}CHR'' \xrightarrow{[RhCl(P^iPr_3)_2]} RR'C{=}CHCH_2R'' \quad (45)$$

Turnover numbers can be as high as 515. For example 9-diazofluorene can be coupled with ethene, propene or styrene. Diphenyldiazomethane can be coupled with ethene to give 1,1-diphenylpropene.

15.2. Oligomerisation and polymerisation reactions

$[RhCl(cod)(PEt_3)]$ catalyses the polymerisation of methylacetylene and phenylacetylene to linear polymers at room temperature. The complex is not as effective as $[RhCl(cod)(PPh_3)]$ and $[RhPh(cod)(PPh_3)]$ [197].

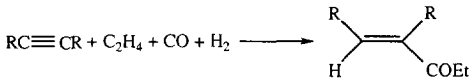
Polysilanes for use in solar cells can be obtained by the polymerisation of 1-silylhexane (Eq. (46)) [198].



(46)

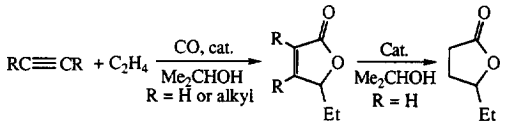
15.3. Formation of oxygenates

Alkynes and ethene can be coupled and carbonylated over a rhodium–trialkylphosphine catalyst to give a variety of products [199]. Using H_2 as the hydrogen source unsaturated ketones are formed (Eq. (47)).



(47)

If an alcohol is employed as the hydrogen source, then the reaction changes to give the unsaturated cyclic lactone shown in Eq. (48). Further reduction *via* transfer hydrogenation to give a γ-caprolactone (also shown in Eq. (48)) can occur.



(48)

A systematic study on the effects of different phosphines on the system was undertaken. The system comprised $[Rh_4(CO)_{12}]$ and phosphine in a secondary alcohol. More basic phosphines (than PPh_3) reduced the activity of the catalyst (PEt_3 gave 18 turnovers (Rh atom)$^{-1}$ h^{-1}, PPh_3 gave 108 turnovers (Rh atom)$^{-1}$ h^{-1} and also suppressed the secondary hydrogenation step. PEt_3 gave a ratio of furanone : lactone of 8 : 1, whilst for PPh_3 the ratio was 1 : 107). The mechanism shown in Fig. 16 has been proposed [199].

CO_2 reacts with butadiene in the presence of a rhodium–phosphine system to produce the furanone, possibly by the mechanism shown in Fig. 17. $[Rh(acac)(CH_2{=}CH_2)_2]$ in the presence of PEt_3 proved to be the best catalyst for the transformation [200]. The only problem with the mechanism shown in Fig. 17 is that for rhodium to be in the usual +3 oxidation state, L must be anionic. The only anionic ligand present is acac, but the 18e$^-$ rule requires that it must only be unidentate, a most unusual coordination mode for acac.

16. Summary

From the results described above, it is clear that trialkylphosphine complexes of rhodium have significant potential in a variety of homogeneously catalysed processes,

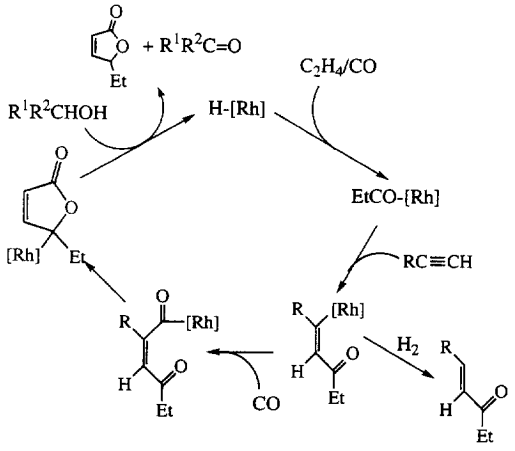


Fig. 16. Proposed mechanism for the condensation of ethene with alkynes and CO in the presence of 2-methylpropan-1-ol catalysed by $[Rh_4(CO)_{12}]$–PR_3. [Rh] = $Rh(CO)_2(PR_3)$, R = Et or Ph [198].

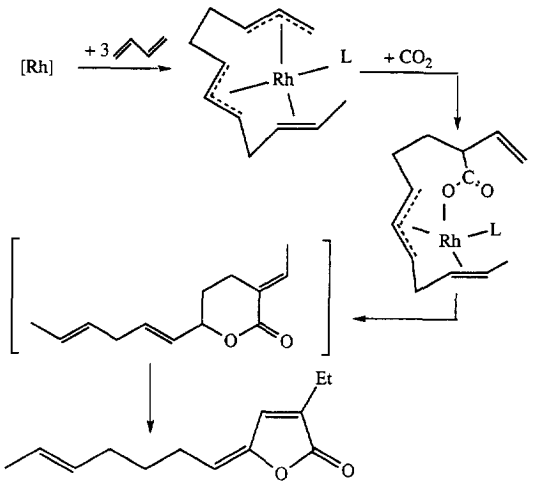


Fig. 17. Proposed mechanism for the condensation of 1,3-butadiene with CO_2 in the presence of a catalyst prepared *in situ* from $[Rh(acac)(C_2H_4)_2]$ and PEt_3 [199].

particularly when oxidative addition (sometimes of difficult substrates) is a key step in the catalytic process. As yet, no processes based on these types of catalyst have been commercialised, but with the different activities and selectivities that are observed, and since there is significant industrial experience in handling cobalt-based systems containing trialkylphosphines, it seems unlikely that this state of affairs will continue for very long.

Acknowledgements

We thank BP Chemicals and the EPSRC for a studentship (MCS) and all our colleagues and co-workers for allowing their results to be used in this review.

Appendix: abbreviations

Ac	acetyl
cod	1,5-cyclooctadiene
Cy	cyclohexyl
Oc	octyl
Pe	pentyl
u.v.	ultra-violet
diop	2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
acac	2,4-pentanedionato
cot	cyclooctene
Et	ethyl
Pr	propyl

thf	tetrahydrofuran
Cp	η^5-cyclopentadienyl
cat	catecholate
nbd	norbornadiene
Bu	butyl
Ph	phenyl
i.r.	infra-red

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