Journal of Organometallic Chemistry, 289 (1985) 385–395
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

METHANOL AS A HYDROGEN DONOR IN REACTIONS HOMOGENEOUSLY CATALYSED BY RUTHENIUM AND RHODIUM COMPLEXES

THOMAS A. SMITH and PETER M. MAITLIS*
Department of Chemistry, The University, Sheffield S3 7HF (Great Britain)

(Received January 28th, 1985)

Summary

Under suitable conditions methanol can act as a hydrogen donor towards organic substrates, especially for the reduction of ketones to alcohols. A variety of complexes of rhodium, iridium, ruthenium, and osmium have been shown to be active for this reaction; the highest activity observed so far is that of t-phosphine-ruthenium-chloride systems such as $[Ru(PPh_3)_3Cl_2]$. In all the reactions the methanol is oxidised to methyl formate; some carbon dioxide is also formed. Cyclohexanone is reduced to cyclohexanol, methyl vinyl ketone and mesityl oxide to the corresponding saturated ketones, and 4-t-butylcyclohexanone to a 4/1 mixture of the *trans* and *cis* 4-t-butylcyclohexanols; aldehydes are reduced with more difficulty and cyclohexene is comparatively unreactive. Possible mechanisms for the reaction are discussed in the light of observations of changes in the catalyst precursors that take place during the reactions. The reactions with methanol are also contrasted with those in which ethanol is used as hydrogen donor.

Introduction

The emergence of methanol as a cheap and plentiful commodity chemical [1] has focussed interest in transformations in which it can participate. In most of these the methanol acts as a source of either hydrogen or carbon monoxide or both, and can thus be regarded as a very convenient source of these materials. The point concerning hydrogen can best be appreciated if it is noted that although the solubility of H_2 in methanol is only around 0.003 mol l^{-1} at 20°C and 1 atm (and hence 0.3 mol l^{-1} at 100 atm) [2], 1 l of methanol can in principle yield no less than 49.4 mol of H_2, by a reversal of the formation reaction (eq. 1). Thus methanol could be an exceedingly useful source of hydrogen; from many points of view it is even better than hydrogen gas itself for hydrogenation reactions, since it is more easily handled and since the local concentration of reductant in a reaction in homogeneous solution can be

0022-328X/85/$03.30

several orders of magnitude higher.

$$CH_3OH \rightleftharpoons CO + 2H_2 \qquad (1)$$

Unfortunately the thermodynamics of reaction 1 are very unfavourable [ΔH^0 (298 K) +91 kJ mol^{-1}] [3] and therefore in order to utilise eq. 1 it must be coupled to a thermodynamically strongly "downhill" reaction. Examples of such processes are hydrogenations and hence we sought to determine whether such hydrogen transfers from methanol to an organic acceptor could be accomplished homogeneously in solution using transition metal complexes as catalysts.

Although higher alcohols [4] (in particular secondary [5] and benzylic alcohols [6]) are well-known as hydrogen donors in hydrogen-transfer reactions, there have only been a few reports of the use of methanol as a source of hydrogen in homogeneously catalysed reactions [7–9]; most workers have in fact assumed it to be an inert solvent. However, recently, since this work was completed, Farnetti et al. have described the use of methanol as a source of hydrogen in a slow hydrogenation of benzylideneacetone, catalysed by phenanthroline-iridium complexes [10]. An earlier study by Imai et al. [6c] of the reduction of cycloheptene by various alcohols in toluene catalysed by $[RhH(PPh_3)_4]$ showed the relative rates to be, propan-2-ol (1100) > ethanol (46) > methanol (6), the last reacting so slowly as to be essentially ineffective as a hydrogen donor. In none of these reactions was any methanol oxidation product identified.

$$RR'CHOH + \text{cyclohexanone} \rightleftharpoons RR'C{=}O + \text{cyclohexanol} \qquad (2)$$

It should be noted that for typical hydrogen transfer reactions such as those defined by eq. 2, while the thermodynamics are favourable for propan-2-ol [R = R' = Me, ΔH^0(298 K) −25.9 kJ mol^{-1}], they become increasingly less favourable for ethanol, n-propanol, and methanol [ΔH^0(298 K) −3.8, +1.3, and +21.0 kJ mol^{-1}, respectively]. This no doubt accounts for the lack of attempts to use methanol as a hydrogen donor.

We describe here the use of methanol as a source of hydrogen for the reduction of a variety of ketones, catalysed by triphenylphosphine ruthenium complexes. Preliminary accounts of this work have been given [11].

Results and discussion

Preliminary experiments using ethanol as hydrogen donor

Since reductions involving methanol were clearly not going to be easy, experiments with ethanol as hydrogen donor were conducted to allow an initial evaluation of catalysts. Cyclohexanone was used as acceptor, and the reactions were run for 5 h at 150°C in Fisher-Porter tubes. As Table 1 shows, triphenylphosphinerhodium catalysts were either ineffective or showed poor turnover numbers; this lack of activity also applied to $[RhCl(P(OPh)_3)_3]$, $[Rh(CO)_2I_2]^-$, $[RhCl(AsPh_3)_3]$, and $[IrCO(Cl)(PPh_3)_2]$; $[Ru(CO)_2Cl_2]$ and $[(areneRu)_2Cl_4]$ showed the formation of low amounts of products. In contrast, high turnover numbers of the products, cyclohexanol and acetaldehyde (eq. 3), were obtained when $[RuCl_2(PPh_3)_3]$ (**1**), $[(C_5Me_5M)_2Cl_4]$ (**2a**, M = Rh; **2b**, M = Ir), and especially $[(C_5Me_5Rh)_2(OH)_3]^+$ (**3**) were used as catalyst precursors.

$$C_6H_{10}O + CH_3CH_2OH \rightleftharpoons C_6H_{11}OH + CH_3CHO \qquad (3)$$

TABLE 1

CATALYSTS FOR THE REACTION OF ETHANOL AND CYCLOHEXANONE [a]

Catalyst	Products [mmol; (turnover number)]	
	Cyclohexanol	Acetaldehyde [b]
[(*p*-cymeneRu)$_2$Cl$_4$]	1.5 (19)	0.1 (1)
[(C$_6$Me$_6$Ru)$_2$Cl$_4$]	0.3 (4)	0.1 (1)
RuCl$_3$·hydrate	0.3 (4)	0.1 (1)
RuCl$_3$·hydrate + 3PPh$_3$	5.5 (69)	0.1 (1)
[RuCl$_2$(PPh$_3$)$_3$]	7.3 (91)	1.6 (20)
[Ru(CO)$_2$Cl$_2$]	0.3 (4)	tr
[RhH(PPh$_3$)$_3$CO]	0.5 (6)	0.3 (4)
[(C$_5$Me$_5$Rh)$_2$Cl$_4$]	6.4 (80)	3.0 (37)
[(C$_5$Me$_5$Rh)$_2$(OH)$_3$]Cl	6.9 (86)	3.3 (41)
[(C$_5$Me$_5$Ir)$_2$Cl$_4$]	7.4 (93)	0.9 (11)

[a] Conditions: cyclohexanone (8 mmol), ethanol (158 mmol) and catalyst (0.08 mmol) at 150°C/5 h. Analysis by GC (6% PEG 20M on Carbopak B) and GC-MS. [b] This is only free acetaldehyde; 1,1-dimethoxyethane was the major product (ratio ca. 3/1).

The amount of free acetaldehyde formed was never equal to that of cyclohexanol, and most was present as 1,1-diethoxyethane (as is to be expected in ethanol solvent), a typical ratio being ca. 1/3. GC-MS analysis also revealed the presence of small amounts of other by-products including acetic acid and ethyl acetate.

Evaluation of catalysts for methanol as hydrogen donor

Since the tri-μ-hydroxydirhodium complex **3** was one of the most active catalysts for the reactions involving ethanol, some experiments with this as catalyst were initially carried out. However, using methanol and cyclohexanone under the same conditions as for the ethanol reactions, only ca. 10% of the amount of cyclohexanol formed there was obtained with methanol as hydrogen donor (Table 2). Addition of either base (triethylamine) or acid (Nafion resin) to the cyclohexanone reactions gave no improvement. Other ketones (PhCOMe, Me$_2$CO) gave similar lowish turnovers; only with methyl vinyl ketone as substrate was a reasonable turnover, to butan-2-one, observed. Cyclohexene gave only a very poor yield of cyclohexane (Table 3).

The most interesting feature of these experiments using [(C$_5$Me$_5$Rh)$_2$(OH)$_3$]Cl (**3**) as catalyst was the observation that the methanol oxidation product was, in all cases, methyl formate. Neither methoxymethanol nor dimethoxymethane, which would be expected if free formaldehyde were intermediate in the reactions, were significant. However, condensation products such as methoxycyclohexene or 1,1-dimethoxycyclohexane, from reaction of cyclohexanone with methanol, were identified as by-products.

The pentamethylcyclopentadienyl-rhodium and -iridium chloro complexes (**2a** and **2b**) had similar activities for promoting the reaction between cyclohexanone and methanol to that of **3**, but the most active catalysts were ruthenium-based (Table 2). Areneruthenium complexes and commercial "ruthenium trichloride hydrate" showed low activity but catalysts made up from ruthenium trichloride and triphenylphosphine or tris(triphenylphosphine)ruthenium(II) complexes showed good activity and gave substantial amounts of cyclohexanol. Again the major methanol oxidation

TABLE 2

CATALYSTS FOR THE REACTION OF METHANOL AND CYCLOHEXANONE

Catalyst	Conditions [a]	Products [mmol; (turnover number)]		
		Cyclohexanol	Methyl formate	Dimethoxy-methane
$[(C_5Me_5Rh)_2(OH)_3]Cl$	A	4.1 (8)	2.0 (4)	0
$[(C_5Me_5Rh)_2(OH)_3]Cl + Et_3N$ [b]	A	3.2 (7)	1.0 (2)	0
$[(C_5Me_5Rh)_2(OH)_3]Cl + H_2O$ [c]	A	2.4 (5)	0.3 (0.5)	0
$[(C_5Me_5Rh)_2(OH)_3]Cl$ + Nafion [d]	A	2.1 (4)	0.4 (1)	0
$[(C_5Me_5Rh)_2(OH)_3]Cl$	B	0.6 (8)	0.7 (9)	0
$[(C_5Me_5Rh)_2Cl_4]$	B	1.1 (14)	1.3 (16)	0
$[(C_5Me_5Ir)_2Cl_4]$	B	1.2 (15)	tr	tr
$[(C_6Me_6Ru)_2Cl_4]$	B	0.5 (6)	tr	tr
$RuCl_3$·hydrate	B	tr	tr	tr
$RuCl_3$·hydrate + PPh_3 [e]	B	tr	tr	tr
$RuCl_3$·hydrate + PPh_3 [f]	B	1.0 (13)	0.4 (5)	1.0 (12)
$RuCl_3$·hydrate + PPh_3 [g]	B	6.5 (81)	2.4 (30)	0.4 (5)
$[RuCl_2(PPh_3)_3]$	B	6.9 (86)	2.4 (30)	0.2 (3)
$[Ru(PPh_3)_3H(Cl)CO]$	B	6.7 (84)	3.4 (42)	0.2 (3)
$[Ru(PPh_3)_3H_2CO]$	B	7.5 (93)	2.4 (30)	0.2 (3)
$[Ru(PPh_3P)_2Cl_2(CO)_2]$	B	1.6 (20)	1.2 (15)	0.8 (11)
$[Os(PPh_3)_3H(Br)CO]$	B	2.0 (25)	tr	tr
$[RuCl_2(PPh_3)_3]$	C	1.0 (13)	0.9 (12)	0.2 (3)

[a] A = Cyclohexanone (48 mmol), catalyst (0.48 mmol) in methanol (1200 mmol) heated (150°C)/5 h under nitrogen (60 atm). B = Cyclohexanone (8 mmol), catalyst (0.08 mmol) in methanol (196 mmol) were heated (150°C/18 h). C = As B except that reactants were heated at 122°C/18 h. [b] Et_3N (4.8 mmol). [c] H_2O (5 cm^3). [d] Nafion resin (0.5 g). [e] PPh_3 (0.08 mmol). [f] PPh_3 (0.16 mmol). [g] PPh_3 (0.24 mmol).

product was methyl formate but, in these cases, it was sometimes accompanied by some dimethoxymethane.

Optimum activity was shown by complex **1** at temperatures of 150 ± 5°C. However, $[Ru(PPh_3)_3H_2CO]$ (**4**), $[Ru(PPh_3)_3H(Cl)CO]$ (**5**), or triphenylphosphine plus ruthenium trichloride hydrate mixtures, with the ratio at least 3/1, gave similar turnovers. Addition of more PPh_3 to complex **1** gave no improvement, while addition of base (triethylamine) caused a significant decrease in yield. Ratios of PPh_3 to Ru lower than 3/1 or $[Ru(Ph_3P)_2Cl_2(CO)_2]$ (**6**) gave substantially lower yields both of cyclohexanol and methyl formate. Reactions were negligibly slow below ca. 150°C, but above ca. 160°C decomposition of catalyst became significant and yields decreased again. In all these reactions a small amount of dimethoxymethane, typically 10% of the methyl formate produced, was also formed.

Triruthenium dodecacarbonyl alone was a poor catalyst (Table 4), but it was steadily improved by the addition of up to 3 molar equivalents of PPh_3 per Ru; the activity at this point was ca. half of that of the best catalyst system, complex **1** or its equivalent. Addition of chloride (as LiCl) to the isolated (but only moderately active) catalyst precursor $[Ru(PPh_3)_2(CO)_3]$, gave another steady increase in activity, up to the point where it was nearly as effective as complex **1**, when ten equivalents had been added.

TABLE 3

REDUCTION OF VARIOUS ORGANIC COMPOUNDS BY METHANOL

Catalyst	Conditions [a]	Products [mmol (turnover numbers)]			
		Alcohol (etc.)		Methyl formate	Dimethoxymethane
PhCOMe	A	PhCHOHMe,	0.8 (7)	tr	0
PhCOMe	B	PhCHOHMe,	4.5 (56)	1.8 (23)	0.3 (4)
4-t-butylcyclohexanone	A	4-t-butylcyclohexanol (*trans*/*cis*, 4/1)	tr	0	0
	B		6.2 (77)	0.7 (9)	0
cyclohexene	A	cyclohexane	0.8 (2)	0.4 (1)	
		+ benzene	tr		
cyclohexene	B	cyclohexane	0.2 (4)	tr	tr
MeCOMe	A	MeCHOHMe	1.4 (3)	1.0 (2)	0
MeCOEt	B	MeCHOHEt	2.1 (27)	2.9 (36)	1.0 (13)
$MeCOCH{=}CH_2$	A	MeCOEt	2.5 (52)	12 (25)	
		+ MeCHOHEt	tr		
$Me_2C{=}CHCOMe$	B	Me_2CHCH_2COMe	5.7 (72)	1.3 (17)	0.1 (2)
MeCHO	A	EtOH	19.7 (41)	0	0
		+ MeOAc	18.7 (39)		
PhCHO	B	$PhCH_2OH$	1.4 (17)	tr	0

[a] A = Catalyst, $[(C_5Me_5Rh)_2(OH)_3]Cl$ (0.48 mmol), substrate (48 mmol) and methanol (1200 mmol) heated at 150°C/5 h under nitrogen (60 atm). B = Catalyst, $[RuCl_2(PPh_3)_3]$ (0.08 mmol), substrate (8 mmol) and methanol (196 mmol) heated at 150°C/18 h.

Reduction of various compounds by methanol and $[RuCl_2(PPh_3)_3]$

Although no exhaustive screening of potential hydrogen acceptors was carried out, Table 3 shows the results from a selection of organic molecules. Thus, under comparable conditions, cyclohexanone and 4-t-butylcyclohexanone gave similar

TABLE 4

EFFECT OF CHLORIDE ON RUTHENIUM CATALYSTS FOR THE REACTION OF METHANOL AND CYCLOHEXANONE [a]

Catalyst	Products [mmol (turnover numbers)]		
	Cyclohexanol	Methyl formate	Dimethoxymethane
$[Ru_3(CO)_{12}]$	0.6 (8)	0	0
$[Ru_3(CO)_{12}]$	0.6 (8)	0	0
$[Ru_3(CO)_{12}]+3PPh_3$ [b]	1.0 (13)	0	0
$[Ru_3(CO)_{12}]+9PPh_3$ [c]	3.5 (44)	1.1 (14)	0.1 (1)
$[Ru(CO)_3(PPh_3)_2]$	2.7 (34)	1.7 (21)	0
$[Ru(CO)_3(PPh_3)_2]+LiCl$ [d]	2.9 (37)	2.0 (25)	0
$[Ru(CO)_3(PPh_3)_2]+2LiCl$ [e]	4.0 (50)	2.3 (29)	0
$[Ru(CO)_3(PPh_3)_2]+10LiCl$ [f]	5.6 (71)	2.5 (31)	0

[a] Conditions: cyclohexanone (8 mmol), catalyst (0.08 mmol) and methanol (196 mmol) heated at 150°C/18 h. [b] PPh_3 (0.24 mmol). [c] PPh_3 (0.72 mmol). [d] LiCl (0.08 mmol). [e] LiCl (0.16 mmol). [f] LiCl (0.8 mmol).

amounts of the cyclohexanols; the ratio of *trans/cis* 4-t-butylcyclohexanols was 4, in agreement with the expected higher stability of the *trans* isomer. Mesityl oxide was easily reduced to 4-methylpentan-2-one in comparable amount, and this was greater than the formation of 1-phenylethanol from acetophenone. Although butan-2-one and benzaldehyde were rather poor hydrogen acceptors under these conditions, modest turnovers of the appropriate alcohols were achieved. Cyclohexene was the poorest acceptor of all, reduction only just being significant after 18 h.

In all cases at least some methyl formate was produced and there was broadly an increase in methyl formate formed which paralleled the increase in amount of reduction product. Again, small amounts of dimethoxymethane were found, and the amount of this seemed to bear some relation to the amount of methyl formate produced. However, it is probably over-ambitious at this stage to expect too close a materials balance since carbon dioxide (see below) was also formed in the overall reaction.

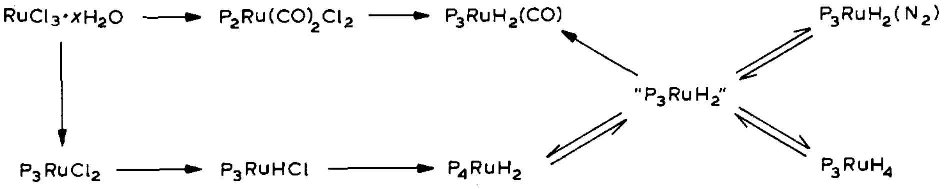
Changes in catalyst precursor [$RuCl_2(PPh_3)_3$] during the reaction

In order to find out more about the species present and the conditions under which products begin to be formed, reactions of methanol and cyclohexanone were carried out under identical conditions but with different times of heating at different temperatures. In each case, complex **1** was used as catalyst precursor, and the contents of the Fisher-Porter tube were analysed by IR spectroscopy (in the region 1750–2400 cm^{-1}) as well as by GC. The IR measurements were made using a data-station which was programmed to subtract automatically peaks due to the solvent and reactants.

We observed three stages in the reaction. (a) The initial brown suspension of **1** slowly dissolved on heating to 110°C to give a red solution; after 0.55 h at this temperature, this solution contained no organic products (by GC analysis), or new IR bands in the 1750–2400 cm^{-1} region. (b) After 0.75 h at 130°C the colour of the solution was brown-yellow, there were still no new bands in the IR (1750–2400 cm^{-1}), and no organic products had yet been formed. (c) Finally, after 1 h at 150°C the colour of the solution was yellow, and it showed the presence of a small amount of cyclohexanol, as well as a band in the IR at 1977 cm^{-1}. Further reaction at that temperature gave steadily increasing amounts of cyclohexanol, together with increasing amounts of methyl formate.

In some the reactions it was possible to isolate solids at the end. These all showed the presence of ruthenium bound carbonyls in their IR spectra; in one case the IR was close to that for [$Ru(PPh_3)_3(H)_2CO$], complex **4**, [ν(CO) 1940, ν(Ru–H) 1898, 1960 cm^{-1}] [12], in another it contained bands which may be assigned to [$Ru(PPh_3)_2Cl_2(CO)_2$] [ν(CO) 1996, 2020 cm^{-1}] [12]. Clearly a number of closely related and labile species are formed in these reactions and the nature of the material isolated depends on the precise conditions used. This is the subject of continuing investigations.

It is also intriguing to speculate that the chief ruthenium species present under conditions (a) and (b) are [$Ru(PPh_3)_3(H)Cl$] [13] and [$Ru(PPh_3)_3(H)_2$] [14] respectively, based on the colours we observed and on the properties reported by others when carrying out related experiments with other alcohols and [$RuCl_2(PPh_3)_3$]. Scheme 1 summarises some of the key complexes that have been isolated and identified as resulting from such reactions. However, our most significant finding is



(P = Ph$_3$P)

SCHEME 1

that no catalytic reaction seems to occur until a ruthenium carbonyl complex is detectable.

At the end of the reaction another band, at 2333 cm^{-1}, was observed in the IR region examined. This was shown to arise from the presence of carbon dioxide in the solution. On standing, the band gradually disappeared, but it increased on addition of small amounts of carbon dioxide. GC analysis also showed the solution and the gas phase to contain carbon dioxide; only trace amounts of other gases such as methane, carbon monoxide, or hydrogen were usually detected. The absence of methane indicates, that the carbon dioxide does not arise by a direct decomposition (eq. 4); it must therefore be formed by a different route, possibly by a water-gas shift reaction, since the data show that methanol can act as a source of CO for ruthenium, at least stoicheiometrically.

$$CH_3OOCH \rightleftharpoons CH_4 + CO_2 \qquad (4)$$

Mechanism of the homogeneously catalysed reactions using methanol as hydrogen donor

It should be noted that although the reaction represented by eq. 1 is thermodynamically very unfavourable, the reaction we have found here (eq. 5), is favourable, with ΔH^0(298 K) ca. -76 kJ mol^{-1}.

$$2CH_3OH + 2(\text{ketone}) \rightleftharpoons CH_3OOCH + 2(\text{alcohol}) \qquad (5)$$

Apparently related reactions in which esters were formed as the oxidation products of alcohols, but only for higher and especially benzylic alcohols, have been reported by Murahashi et al. [15] and by Blum and Shvo [16], e.g.,

$$2PhCH_2OH + 2PhC{\equiv}CPh \rightleftharpoons PhCH_2OOCPh + 2PhCH{=}CHPh$$

However, in this case the best catalyst system appears to be $[Ru_3(CO)_{12}]$.

We consider three possible reaction paths that may be taken when the methanol reacts with the catalyst and subsequently reduces the ketone, eqs. 6, 7 and 8.

(A) Via hydrido-formato complexes

$$CH_3OH + H_2O + M_n \rightarrow M_n(H)_m(O_2CH)$$

$$M_n(H)_m(O_2CH) + MeOH + m/2{>}C{=}O \rightarrow M_n + MeOOCH + m/2{>}CHOH \qquad (6)$$

In reaction 6 a redox process occurs in which methanol and water (certainly present in small amount at least) react to give a metal formato-hydride complex. This may well require two or more metal atoms to participate. An analogue of this reaction has been described by Nutton et al., in which complex **3** reacts with ethanol to give hydrido-acetatodirhodium complexes [17].

$$C_2H_5OH + [(C_5Me_5Rh)_2(OH)_3]^+ \rightarrow [(C_5Me_5Rh)_2(\mu\text{-}H)_x(\mu\text{-}O_2CMe)_{3-x}]^+$$

$(x = 1 \text{ or } 2)$

Unfortunately attempts to test this proposal by synthesising the μ-formato-di-μ-hydrido complex, $[(C_5Me_5Rh)_2(\mu\text{-}H)_2(\mu\text{-}OCHO)]$ [18], and reacting it with methanol were unsuccessful since the complex was very unstable; only traces of methyl formate were obtained. Instead we noted that, when solutions of the tri-μ-hydroxo-dirhodium complex **3** were reacted with methanol alone, a series of colour changes occurred which paralleled those previously found where **3** was reacted with propan-2-ol and which were found to lead first to the deep red trinuclear oxytrihydride, $[(C_5Me_5Rh)_3(H)_3O]^+$ [19], and then to the dark green tetranuclear tetrahydride dication, $[(C_5Me_5Rh)_4(H)_4]^{2+}$ [18]. Indeed, this reaction suggests that the path via a formato complex intermediate is not operative. Further, since formaldehyde is known to disproportionate in solutions containing **3** (to methanol, formic acid and formate complexes [18,20]) it seems unlikely that the reaction described here proceeds via free formaldehyde either.

(B) Via carbonyl-hydride complexes

$$CH_3OH + M_n \rightarrow M_n(H)_xCO \qquad (7)$$

The reaction schematically illustrated by eq. 7 implies the methanol to be completely split by the metal (which can be a mono- or poly-nuclear complex) into coordinated CO and hydrogen (at least part of which is present as coordinated hydride). The coordinated hydride is then available for reduction by the ketone, as before. The route from coordinated carbonyl to methyl formate is not quite so clear, but methoxide is known to add easily to coordinated CO forming MCOOMe [21]. Further, ruthenium complexes have been reported to promote the reaction of methanol with CO to give methyl formate [22].

The fact that in the ruthenium-catalysed reactions of methanol and cyclohexanone no organic products are seen until the formation of a carbonyl complex, suggests that coordinated carbonyl must play a vital role in the overall process and lends support to such a mechanism.

As a model for part of this reaction, we may note that Chatt et al. already in 1964 reported that phosphine ruthenium chloride complexes formed carbonyls on reaction with higher alcohols, e.g., ethanol gave methane and a ruthenium carbonyl [23].

(C) Via formaldehyde-hydride complexes

The third possibility, described by eq. 8, implies that the methanol is split into

$$CH_3OH + M_n \rightleftharpoons M_n(CH_2O)(H)_2 \qquad (8)$$

two hydrides and one formaldehyde, both coordinated to the metal. Several η^2-formaldehyde complexes are now known [24–26], of particular relevance being the reaction recently described by Green et al. in which methanol is cleaved in precisely the way indicated in eq. 9 by a tungsten complex,

$$[HW(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)] + CH_3OH \rightleftharpoons [H_2W(PMe_3)_4(CH_2{=}O) + PMe_3 \qquad (9)$$

Again, if eq. 8 were to represent the actual path, the hydride formed could directly reduce the ketone. The formation of methyl formate from the coordinated formaldehyde presents some problems, however. If free formaldehyde is formed then, in the presence of methanol, dimethoxymethane (or methoxymethanol), rather than methyl formate should be the product; alternatively, in the presence of our rhodium catalysts, disproportionation would be expected. The fact that only small amounts of dimethoxymethane are detected, and then only in the ruthenium-promoted reactions, suggests that a path involving formaldehyde may not be the most significant one. Given the reaction conditions (small amounts of metal complex catalysts in large amounts of methanol) the direct combination of two η^2-formaldehyde complexes in a bimolecular process to give methyl formate, also seems unlikely.

However, it may be noted that the complex equivalent to "$(Ph_3P)_3Ru(CO)$" reacts with formaldehyde to give a methyl-formato complex, $[(Ph_3P)_2Ru(O_2CH)(CH_3)(CO)]$, possibly via a $RuCH_2OCH_2O$ intermediate [24]. $[Cp_2V(CH_2O)]$ has also been reported to react slowly with paraformaldehyde to give methyl formate; however that reaction was carried out in toluene solution [26].

Conclusion

On the evidence presently available, the mechanism indicated by route 6 seems unlikely. We are not yet able to discriminate completely between paths 7 and 8 but we rather favour the former, involving carbonyl-hydride intermediates, for the major reaction path for the ruthenium complexes. It is also likely that a variation thereof, possibly not involving detectable amounts of metal carbonyls, is the most probable route for the C_5Me_5Rh-promoted reaction too. Exactly what species are involved in the two types of reaction is the subject of continuing investigation.

A secondary path for the ruthenium systems may, because of the detection of dimethoxymethane in some of these reactions, well involve formaldehyde complexes. This is particularly so in view of a recent disclosure that formaldehyde can be produced from methanol on irradiation in the presence of a $Ru_2(OAc)_4Cl$-t-phosphine catalyst [27].

Experimental

Complexes were prepared by standard literature routes, for example, $[(C_5Me_5Rh)_2(OH)_3]Cl$ [28], $[RuCl_2(PPh_3)_3]$ [29], $[Ru(PPh_3)_3H_2CO]$ [12], $[Ru(PPh_3)_3H(Cl)CO]$ [12], and $[Ru(PPh_3)_2(CO)_3]$ [12]. Smaller scale reactions were carried out in thick walled glass tubes ("Fisher-Porter" tubes) which could tolerate a pressure of up to 10 atm at 150°C; the larger scale reactions were carried out in stainless steel autoclaves; only qualitative differences between the two types of reactions were detected and it is concluded that no reactions with the walls of the vessels were occurring. The results of the reactions are detailed, together with the precise conditions used, in Tables 1–4. The products were analysed by GC (Carlo Erba 4100 or Packard 427 chromatographs) and by GC-MS (Kratos MS-25S), and by comparison with authentic samples. Typical conditions for the analysis of solutions from methanol reactions were: 2 m column filled with 6% PEG 20M on Carbopak B, temperature programmed from 80–200°C and 4°C/min. Retention times were, methyl formate (2.0 min), methanol (2.4), dimethoxymethane (3.1), acetone (3.1), propan-2-ol (4.8), cyclohexanone (16.9), cyclohexanol (20.1). Gas analyses were carried out using a Packard 427 chromatograph fitted with a katharometer detector and helium as carrier gas through a 2 m Carbosieve (80/10) column. A programmed run 40–180°C at 4°C/min gave the following retention times: hydrogen (0.6 min), nitrogen (1.6), carbon monoxide (2.1), methane (4.6) and carbon dioxide (10.5).

IR spectra were measured on a Perkin–Elmer 157G spectrometer or, for measurements in methanol solution, on a PE 684 spectrometer coupled to a PE 3600 Data Station programmed to electronically subtract background and solvent peaks.

Acknowledgements

We thank the SERC and BP Chemicals Ltd., Hull, for a CASE Award (to T.A.S.), Johnson Matthey for the loan of ruthenium and iridium salts, Mr. D.G. Andrews and Mr. P.R. Ashton for technical assistance, Dr. J. Cook for discussions, and Mr. A.P. Bushell for preparing the hydrido-formato-dirhodium complexes.

References

1 Chem. Eng. News, July 16 (1984).
2 A. Seidell, Solubilities of Inorganic and Metal Organic Compounds, D. Van Nostrand, New York, 1953, 3rd Edn., Vol. 1, p. 564 et seq.
3 D.R. Stull, E.F. Westrum and G.C. Sinke, The Chemical Thermodynamics of Organic Compounds, J. Wiley, New York, 1969.
4 I.S. Kolomnikov, V.P. Kukolev and M.E. Vol'pin, Russ. Chem. Rev., Engl. Transl., 43 (1974) 399.
5 Y.M.Y. Haddad, H.B. Henbest, J. Husbands and T.R.B. Mitchell, Proc. Chem. Soc., (1964) 361; J. Trocha-Grimshaw and H.B. Henbest, J. Chem. Soc., Chem. Commun., (1967) 544; M. Visintin, R. Spogliarich, J. Kaspar and M. Graziani, J. Mol. Catal., 24 (1984) 277 and references therein; R. Spogliarich, G. Mestroni and M. Graziani, J. Organomet. Chem., 22 (1984) 309 and references therein.
6 (a) G. Gregorio, C. Pregaglia and R. Ugo, Inorg. Chim. Acta., 3 (1969) 89; (b) Y. Sasson and J. Blum, Tetrahedron Letters, (1969) 2167, J. Org. Chem., 40 (1975) 1887; (c) H. Imai, T. Nishiguchi and K. Fukuzumi, ibid., 41 (1976) 665; (d) G. Speier and L. Markó, J. Organomet. Chem., 210 (1981) 253.
7 J.C. Bailar and H. Itatani, J. Am. Chem. Soc., 89 (1967) 1592, 1600; J. Am. Oil Chem. Soc., 43 (1966) 337; ibid., 44 (1967) 147.
8 J.M. Landesberg, L. Katz and C. Olsen, J. Org. Chem., 37 (1972) 930.
9 H. Imai, T. Nishiguchi and K. Fukuzumi, J. Org. Chem., 39 (1974) 1622.
10 E. Farnetti, F. Vinzi and G. Mestroni, J. Mol. Catal., 24 (1984) 147.
11 T.A. Smith and P.M. Maitlis, J. Organomet. Chem., 269 (1984) C7, and P.M. Maitlis, Proc. Fourth Int. Symp. Homogeneous Catal. (Leningrad), in press.
12 N. Ahmad, S.D. Robinson and M.F. Uttley, J. Chem. Soc., Dalton Trans., (1972) 843; N. Ahmad, J.J. Levison, S.D. Robinson and M.F. Uttley, Inorg. Synth., 15 (1974) 48, 50.
13 B.N. Chaudret, D.J. Cole-Hamilton, R.S. Nohr and G. Wilkinson, J. Chem. Soc., Dalton Trans., 1546 (1977); J.J. Levison and S.D. Robinson, J. Chem. Soc. (A), (1970) 2947.
14 J. Collman and W. Roper, J. Am. Chem. Soc., 87 (1965) 4008; T. Ito, S. Kitazume, A. Yamamoto and S. Ikeda, ibid., 92 (1970) 3011; W. Knoth, J. Am. Chem. Soc., 94 (1972) 104; R.O. Harris, N.H. Hota, L. Sadavoy and J.M.C. Yuen, J. Organomet. Chem., 54 (1973) 259.
15 S-I. Murahashi, K-I. Ito, T. Naota and Y. Maeda, Tetrahedron Letters, (1981) 5327.
16 Y. Blum and Y. Shvo, J. Organomet. Chem., 263 (1984) 93.
17 A. Nutton, P.M. Bailey and P.M. Maitlis, J. Organomet. Chem., 213 (1981) 313.
18 J. Cook, J.E. Hamlin, A. Nutton and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1981) 2342.
19 P. Espinet, P.M. Bailey, P. Piraino and P.M. Maitlis, Inorg. Chem., 18 (1979) 2706; J.S. Ricci, T.F. Koetzle, R.J. Goodfellow, P. Espinet and P.M. Maitlis, ibid., 23 (1984) 1828.
20 J. Cook and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1981) 924.

21 See, for example, N. Grice, S.C. Kao and R. Pettit, J. Am. Chem. Soc., 101 (1979) 1627; D. Braga, B.F.G. Johnson, J. Lewis, M. McPartlin, W.J.H. Nelson, J.N. Nicholls and M.D. Vargas, J. Chem. Soc., Chem. Commun., (1982) 966; and D.J. Darensbourg, R.L. Gray and M. Pala, Organometallics, 3 (1984) 1928.
22 D.J. Darensbourg, C. Ovalles and M. Pala, J. Am. Chem. Soc., 105 (1983) 5937.
23 J. Chatt, B.L. Shaw and J. Field, J. Chem. Soc., (1964) 3466.
24 G.R. Clark, C.E.L. Headford, K. Marsden, and W.R. Roper, J. Organomet. Chem., 231 (1982) 335; W.R. Roper and L.J. Wright, J. Organomet. Chem., 234 (1982) C5.
25 M.L.H. Green, G. Parkin, K.J. Moynihan and K. Prout, J. Chem. Soc., Chem. Commun., (1984) 1540.
26 S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Am. Chem. Soc., 104 (1982) 2019.
27 S. Shinoda, H. Itagaki, T. Takahashi, H. Yamamoto and Y. Saito, Proc. 4th Int. Symp. Homogeneous Catal. (Leningrad), 1984, Abstract L10-10.
28 J.W. Kang and P.M. Maitlis, J. Organomet. Chem., 30 (1971) 127.
29 J.A. Osborn and G. Wilkinson, Inorg. Synth., 10 (1969) 68.