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Carbon monoxide activation in homogeneously catalysed reactions: the nature and roles of catalytic promoters†

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One of the outstanding problems and challenges in CO activation concerns the lack of a detailed mechanistic understanding of the roles of catalytic promoters used in a number of homogeneously catalysed carbonylation reactions. These problems, and attempts at their resolution, are highlighted with reference to (i) the varied range of promoters that have found use in composite catalysts for the direct synthesis of oxygenates such as ethylene glycol and ethanol from CO/H_2, (ii) the promotional effects of N-bases in the catalytic methoxycarbonylation of alkenes to esters, and (iii) some preliminary ^{13}C NMR spectroscopic evidence which is enabling the definition of a dual role of Ru-promoters as iodide abstraction agents in the Ir-catalysed carbonylation of methanol to ethanoic (acetic) acid. The detection, and characterisation in solution, of an iodide-bridged Ru–Ir dimer is facilitating the development of a plausible, internally consistent model on which to base the catalysis.

Introduction

From a consideration of the literature concerning the activation of CO, particularly towards the catalytic functionalisation of organic molecules, a common feature that emerges is the observation of so-called ‘promoter’ effects in many of these reactions. Promoters appear in many guises–particularly halides, alkali and alkaline earth metal cations, additional transition metals, N-bases, P-ligands, solvents, *etc.*,–and, frequently more than one is necessary for the operation of the composite catalyst to the required specification. With very few exceptions, the mechanistic understanding underlying these effects is extremely limited. Concerted attempts to address such mechanistic problems could lead to a new generation of homogeneous catalysts for the incorporation of CO into organic molecules. Within the spirit of Dalton Discussion 4, this paper will attempt to address some of these aspects, by a consideration of selected examples of homogeneously catalysed reactions that require promoters for CO activation and, in particular, highlighting unresolved problem areas such as the activation of CO towards direct reduction to oxygenated molecules. Some preliminary new results that are relevant to an understanding of promotional effects of Ru complexes on the Ir-catalysed carbonylation of methanol to acetic acid will also be described.

At the outset it is important to draw the distinction between catalyst promoters and poisons. Not all modifiers act as true promoters, defined for the purpose of this paper as enhancing *both* catalytic activity *and* selectivity to the desired product(s). Frequently, additional ligands such as tertiary phosphines are described as promoters whereas in reality, in hydroformylation for example, they act as selective poisons. The addition of phosphines to the classic Co-catalysed process results in a reduction in catalytic activity by an order of magnitude but with a considerable increase in selectivity to the desired linear isomer of the product aldehyde.[1] Nevertheless, the roles of organophosphines are probably amongst the most well known and understood in mechanistic terms in homogeneous catalysis. In contrast to selective poisoning by tertiary phosphines in hydroformylation, the *true* promotional role exhibited by N-containing bases in enhancing *both* reaction rates *and* selectivities to the desired straight chain products in the Co-catalysed methoxycarbonylation of alkenes has been known for a number of years, although their mechanistic role is still the subject of active debate.[2] The promotional role of halides in the iodide-promoted, Rh-catalysed, carbonylation of methanol to acetic acid, originally developed by Monsanto, is well known and probably the most well understood. Here the origin of the promotional effect of iodide is only indirectly related to CO activation and concerns enhancement of oxidative addition of CH_3I rather than CH_3OH to the Rh(I) centre. Methanol is converted into the more highly electrophilic methyl iodide which is consequently more susceptible to nucleophilic attack by $[Rh^{I}(CO)_2I_2]^-$ *via* oxidative addition to give the Rh(III) methyl complex $[CH_3Rh^{III}(CO)_2I_3]^-$, an intermediate that undergoes rapid migratory insertion of CO to form the corresponding acyl $[Rh^{III}(COCH_3)(CO)_2I_3]^-$ (ref. 3). By contrast, in the most recent development, the Ir-catalysed Cativa (BP Chemicals) process for methanol carbonylation, the kinetic behaviour is significantly different.[4] In particular, the relative rates of the oxidative addition and migratory insertion steps are reversed and, as a consequence, additional catalyst promoters have been required to accelerate the migratory insertion step in order to ensure economic viability.

Direct hydrogenation of CO to oxygenate molecules

One of the outstanding problems and challenges in CO activation concerns the selective reduction of CO to oxygenated molecules such as methanol, ethanol, ethylene glycol and acetic acid. Much of the associated chemistry was investigated 15–20 years ago, under the name C_1 chemistry,[5] and is thus ripe for revisitation. In this previous work particular emphasis was placed on the development of homogeneous catalysts for the production of C_2 molecules such as ethylene glycol, ethanol and ethanoic (acetic) acid; of these, the first product is unique to homogeneous catalysis–there are no known heterogeneous catalysts that can accomplish this transformation:

$$2CO + 3H_2 \longrightarrow HOCH_2CH_2OH$$

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Table 1 Selected homogeneous catalyst compositions for the direct production of oxygenates from synthesis gas

	Catalyst composition						
Product	Metals	Promoter, solvent	Pressure /bar	Temperature /°C	Selectivity (%)	Activity/g l^{-1} h^{-1}	Ref.
CH_3OH	Ni	$[OCH_3]^-$	10–50	80–120	high	128	6, 7
	Ru	I^-	850	230	70	50 (h^{-1})	8
$HOCH_2CH_2OH$	Rh	2-Hydroxypyridine, Cs^+, tetraglyme	550	220	67	15	9
	Rh	PPr^i_3, 1-Methylimidazole, DMI	500	220	80	280	10
	Ru	NMBI, Tetraglyme	500[a]	260	65	125	11
C_2H_5OH	Ru	I_2, Pr^n_3PO	850	230	≈60	180	12
	Co/Ru	KI, NMP, Tetraglyme	850	220	50	35	13
CH_3CO_2H	Co/Ru	Onium bromide, $P(OPh)_3$, toluene	1400	220	80	≈10	14

DMI = 1,3-Dimethyl-2-imidazolidinone, NMBI = *N*-methylbenzimidazole, NMP = *N*-methylpyrrolidone.[a] CO/H_2 ratio 1 : 2; all others 1 : 1.

Table 2 Promoted Ru/Rh catalysts for the production of acetate esters of ethylene glycol directly from synthesis gas (from ref. 15)

Catalyst composition/mmol			Products/mol l^{-1} h^{-1}		Molar selectivity (%)
Ru	Rh	Promoter	Methyl acetate	Ethylene glycol diacetate	(EGOAc/Σ MeOAc + EGOAc)
2.0	—	—	0.180	0.017	8.6
2.0	—	2.0 Et_3N	0.162	0.010	5.8
2.0	—	2.0 Cs^+	0.180	0.020	10.0
—	0.2	—	0.175	0.011	5.9
—	0.2	2.0 Et_3N	0.093	0.128	57.9
—	0.2	2.0 Cs^+	0.084	0.128	60.3
2.0	0.2	—	0.419	0.038	7.8
2.0	0.2	2.0 Et_3N	0.211	0.276	56.7
2.0	0.2	2.0 Cs^+	0.226	0.365	61.8
2.0	0.2	2.0 Cs^{+}[a]	0.340	0.013	3.7

Reaction conditions–solvent: glacial acetic acid (50 ml), pressure: 1000 bar CO/H_2 (1 : 1), temperature: 230 °C, reaction time: 2 h.[a] Solvent tetraglyme, products are methanol and ethylene glycol.

Many homogeneous catalysts have been described for such reactions, and particular interest has focussed on those factors which control C_2/C_1 product selectivities, usually a consequence of the (generally serendipitous) choice of appropriate promoter(s).

A selection of the many composite homogeneous catalyst formulations that have been reported for the direct conversion of synthesis gas into methanol, ethylene glycol, ethanol and acetic acid is summarised in Table 1. Reference to Table 1 highlights the importance of the transition metals Rh, Co and Ru, both alone and in combination; other catalytically important metals, such as Ni, Pd and Pt, are only of relatively minor significance in this area of chemistry. A general pattern that emerges shows that Rh, and Ru/Rh combinations give highest selectivities to ethylene glycol, whereas mixed Co/Ru catalysts are preferable for the direct synthesis of ethanol and acetic acid (and for the hydrocarbonylation of methanol). A feature that is immediately evident is the uniformly high pressure requirement, which has rendered these systems uneconomic in terms of commercial viability at their present state of development. It is also evident that all these catalyst formulations include a number of different types of catalyst promoters listed in the Introduction section; combinations of promoters are frequently required for optimum performance in CO reduction.

The genuine role of catalyst promoters in this type of system can be illustrated with reference to Table 2 in which some of our previous work[15] using composite catalyst formulations for the selective production of C_2-oxygenate esters from synthesis gas using mixed Ru and Rh catalysts is summarised. This illustrates the synergistic effects between Rh and Ru, and the dramatic effect on both catalytic activity and product selectivity, particularly towards the desired ethylene glycol esters, consequent upon the addition of approximately stoichiometric amounts (on catalyst) of nitrogen-containing bases such as triethylamine and/or alkali metal cations, particularly Cs^+. Inspection of Table 2 illustrates that the two metals, Ru and Rh, a promoter (Et_3N and/or Cs^+), and the solvent acetic acid are integral requirements of the composite catalyst for the selective formation of ethylene glycol acetate esters. The minor metal component (Rh) appears to largely determine the product selectivity, whereas the major component (Ru) considerably enhances total activity, possibly by enhancing overall rates of hydrogenation. However, the intimate and important role of the additional promoters remains far from clear.

Reaction mechanisms

One of the intriguing and, as yet incompletely resolved, aspects concerns reaction mechanisms in this chemistry. In particular, that which is the least understood is the initial and most energetically demanding step, namely the mechanism by which carbon monoxide is reduced to the presumed formyl intermediate. Having undergone this transformation the subsequent chemistry can be largely explained in terms of contemporary organometallic chemistry. Plausible mechanistic schemes for the production of the oxygenates methanol, ethylene glycol and polyalcohols from synthesis gas have been developed,[8] although supporting evidence is surprisingly sparse, partly as a consequence of the severe reaction conditions required, particularly the very high pressures (up to 3000 bar). An analysis of the kinetic behaviour of Co catalysts under much lower pressures than the 3000 bar used in early work, and under which conditions the reaction is markedly slower, has proved instructive.[16] The rate equation for product formation shows first order dependences on both Co concentration and P_{H_2} (ref. 17). The major species present in solution during catalysis has been shown to be $HCo(CO)_4$ and the kinetic behaviour has been interpreted in terms of the occurrence of intramolecular hydride migration from the metal to a carbonyl ligand with the formation of a formyl intermediate. It has been reasoned that subsequent reaction of the formyl intermediate with dihydrogen would convert the formyl ligand into coordinated formaldehyde.[17]

$$(CO)_4Co\text{–}H \rightleftharpoons (CO)_3Co\text{–}C(O)H \xrightarrow{H_2} (CO)_3HCo(H_2CO)$$

Although the production of *free* formaldehyde is known to be thermodynamically unfavourable, the intermediate/transient formation of coordinated formaldehyde is plausible,[8] particularly in the presence of additional reagents, *e.g.*, carboxylic acid solvents, which may serve to drive subsequent reactions, such as esterification of hydroxymethyl ligands before final release of product from the coordination sphere of the metal.[15]

The mechanism by which the initial reduction of CO occurs is undoubtedly the least well-defined (and most difficult) of all synthesis gas reactions. In the Ru-catalysed systems the apparent requirement for two specific complexes in solution has led to the suggestion that intermolecular hydride transfer from $[HRu_3(CO)_{11}]^-$ to a carbonyl ligand in $[Ru(CO)_3I_3]^-$ could be involved in the generation of a reactive formyl intermediate.[8]

Pathways through which a transient formaldehyde complex could react to give the observed product distributions are fairly well-defined and illustrated in Fig. 1.[17] The key step in this reaction is the formal insertion of formaldehyde into a metal–hydrogen bond to yield either/or both methoxy and hydroxymethyl species. The former is the likely precursor to methanol (or methyl formate) and the latter can generate glycolaldehyde, and then ethylene glycol, *etc.* The direction of addition is likely to depend on a number of factors, including the relative acidity of the hydride ligand. The use of acetic acid as reaction solvent has also been found to enhance reaction rates *and* selectivities to C_2 products,[15] possibly *via* the intermediate formation of acetate esters of hydroxymethyl ligands, *e.g.* $M\text{–}CH_2OC(O)CH_3$.

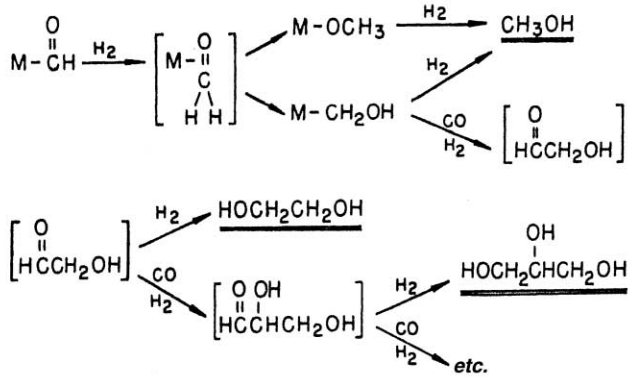

Fig. 1 General mechanistic pathways proposed for oxygenate formation in homogeneously catalysed CO hydrogenation.

However, although some qualitative understanding of the systems detailed in Tables 1 and 2 has emerged, a detailed quantification of the nature of such promoter effects in general remains elusive. The high pressure requirement is undoubtedly an undesired complexity that inhibits detailed and accurate kinetic studies. Nevertheless, the development of an in-depth understanding of some of these promoter effects in carefully selected systems may enable the outstanding 'high pressure' problem to be overcome and a second generation of homogeneous catalysts to be developed for this important area of chemistry.

Cobalt-catalysed methoxycarbonylation of alkenes and dienes

A rather more amenable system for the investigation of promoter effects concerns the N-base promoted, Co-catalysed alkoxycarbonylation of alkenes (and dienes) to esters. This reaction has been of general interest for many years,[1] indeed since the discovery of hydroformylation (the reaction was first discovered by Reppe during the period 1938–1945), and it represents another member in this family of closely related reactions, *viz.*,

$$RCH{=}CH_2 + CO + HX \longrightarrow RCH_2CH_2COX + RCH(COX)CH_3$$

When X = H, OH, OR′ the products are aldehydes (hydroformylation), acids and esters, respectively. Interest in Co-catalysed methoxycarbonylation has focussed on two principal applications, namely (i) as an alternative to hydroformylation for the selective production of long chain detergent range alcohols from alkenes[18] and (ii) for the production of adipic acid, an intermediate in Nylon manufacture, by the selective di(methoxycarbonylation) of buta-1,3-diene to dimethyl adipate, followed by hydrolysis.[19] N-Containing bases have been shown to accelerate the rate of standard Co carbonyl catalysts for the methoxycarbonylation (130 bar pressure, 180 °C) of long chain alkenes to the homologous methyl esters (with high linear/branched product selectivities), which, after hydrolysis, afford the corresponding alcohols.[20] Most importantly, when internal alkenes are used as substrates, the presence of a N-containing base has been found to promote the isomerisation of *internal* to *terminal* alkenes prior to methoxycarbonylation, with consequent enhancement of desired product selectivity. An obvious benefit is thus the capability to alkoxycarbonylate isomeric C_n olefin mixtures without prior fractionation and still obtain good product selectivities to terminally functionalised esters. In a classical catalyst screening exercise, two decades before the advent of 'combinatorial chemistry', 300 combinations of Group VIII non-noble metals (Fe, Co and Ni) and halogen free promoters (N, P, As, Sb, O, and S) were examined as catalysts for this reaction. The outcome was the identification of optimum catalyst combinations comprising Co/pyridine or Co/4-methylpyridine (4-picoline) which gave esters of high linearity ($\geq$ 75%) and selectivities of $\geq$ 95%. A comparison between methoxycarbonylation and two different hydroformylation processes (Co, Co/P) demonstrated that the former could provide an economically viable alternative for the production of long chain alcohols and acids.[18]

The second example of methoxycarbonylation technology concerns the long sought after *selective* di-carbonylation of buta-1,3-diene to adipic acid.[19] Research at BASF led to the development of a two-stage process, *via* methyl-3-pentenoate (obtained in 90% selectivity), for the conversion of buta-1,3-diene, CO and methanol to the dimethyl ester of adipic acid, also using pyridine-promoted Co carbonyl catalysts. In the second stage, isomerisation of the 3- to 4-pentenoic acid ester is a pre-requisite for the subsequent carbonylation to give dimethyl adipate with an overall selectivity of 70% (ref. 21).

Reaction mechanisms

Although little accurate kinetic information on these reactions is available in the open literature, plausible mechanistic reaction sequences have been developed,[22–24] and the role of both hydride and methoxycarbonyl mechanistic pathways has been considered. Indeed, DuPont authors prefer a mechanism which involves the synergistic operation of both alkoxycarbonyl and hydridocobalt pathways, in which addition of the alkoxycarbonyl complex to the alkene is preferred (Fig. 2). Nevertheless $ROC(O)Co(CO)_4$, [ν(CO) *ca.* 2119, 2046, 2028 and 1685 cm^{-1}] prepared *in situ* from the reaction of CO (100 bar, room temperature) with $[pyH][Co(CO)_4]$, or $Co_2(CO)_8$ and pyridine $\{[Copy_6][Co(CO)_4]_2\}$, in EtOH or Pr^iOH, is surprisingly stable in the presence of an alkene such as hept-1-ene, negligible reaction occurring below 170 °C under CO pressure.[25] In general, there is relatively little definitive experimental evidence

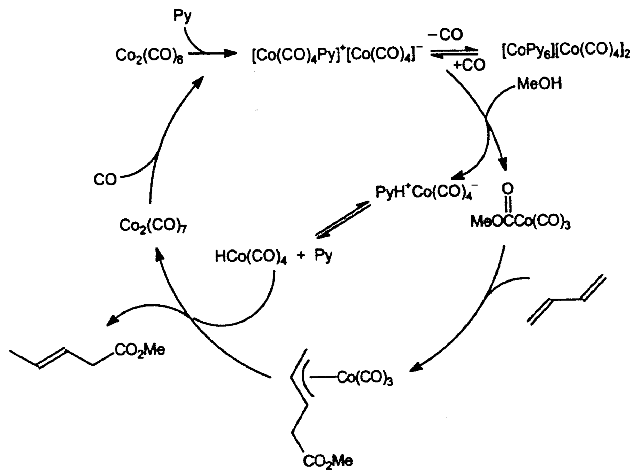

Fig. 2 The 'methoxycarbonyl' pathway proposed for the Co-catalysed conversion of buta-1,3-diene, and alkenes in general, to esters.

in support of mechanistic pathways, largely because of the lack of readily available spectrosopic 'handles' to monitor metal complex speciation in solution under reaction conditions. The mechanistic role played by the N-containing base promoters in particular is the subject of active debate, including the role of the equilibrium

$$[pyH][Co(CO)_4] \rightleftharpoons py + HCo(CO)_4$$

and the involvement of purported acylpyridinium cobalt carbonyl intermediates such as $[RCOpy]^+[Co(CO)_4]^-$, which, in enhancing the rate-limiting alcoholysis of acyl carbonyls, have been described as 'second level' accelerators of the overall methoxycarbonylation reaction:[2]

$$RCH_2CH_2C(O)Co(CO)_4 \xrightarrow{C_5H_5N} [RCH_2CH_2C(O)NC_5H_5]^+[Co(CO)_4]^- \xrightarrow{CH_3OH} RCH_2CH_2C(O)OCH_3 + HCo(CO)_4 + C_5H_5N$$

Thus an appropriate combination of *neutral* and *ionic* intermediates can be envisaged to provide optimum performance in the catalytic cycle.

Finally, in view of the generally high activity associated with the use of Rh catalysts in carbonylation chemistry (*cf.* hydroformylation, methanol carbonylation and ethylene glycol synthesis), it is remarkable that equivalent Rh/N-base catalyst combinations should be completely inactive towards methoxycarbonylation of alkenes under comparable conditions to those used with Co catalysts;[26] rapid isomerisation of terminal to internal alkenes is observed, and $[Rh_5(CO)_{15}]^-$ has been detected as a major Rh carbonyl-containing species present in solution by *in situ* high pressure IR spectroscopy.[26] There appear to be no published reports of Rh alkoxycarbonylation catalysts that are analogous to their Co counterparts. The fundamental differences between the two metals may reside in the lower acidity of potential Rh-containing intermediates relative to the well-known high acidity associated with $HCo(CO)_4$ (ref. 27). The incorporation of acidic catalyst promoters, combined with a more complete understanding of the role of the N-containing base promoters, may enable these mechanistic anomalies to be fully resolved and a range of active homogeneous Rh catalysts for alkoxycarbonylation to be discovered and developed.

Promotion, by Ru, of the Ir-catalysed process for the carbonylation of methanol to acetic acid

Since the early 1970s all new processes for the manufacture of acetic acid (and acetyl chemicals) have used C_1 feedstocks such as CH_3OH, and homogeneous carbonylation-based technology, which rapidly superseded previous petrochemical based production routes, *e.g.*, ethylene oxidation.[28] Homogeneously catalysed processes for methanol carbonylation include a high-pressure version, using halide-promoted Co catalysts,[29] developed by BASF in 1966, and the much lower pressure iodide-promoted Rh- and Ir-based processes, introduced by Monsanto in 1970 (ref. 30) and BP Chemicals in 1996 (ref. 4), respectively (see Table 3). As indicated in the Introduction the technology associated with the Rh-catalysed carbonylation of methanol to acetic acid in particular is both well established and well understood in chemical terms.[3]

The principal role played by iodide as a catalytic 'promoter' in each system is in the conversion of methanol to the more highly electrophilic methyl iodide:

$$CH_3OH + HI \rightarrow CH_3I + H_2O$$

and that of the organometallic catalyst is the promotion of oxidative addition and/or migratory insertion of CO, with the net effect of increasing the carbon number of the reacting substrate, CH_3I, by one:

$$CH_3I + CO \xrightarrow{[M]} CH_3C(O)I \quad M = Co, Rh, Ir$$

Reaction mechanisms

The kinetic behaviour of the three processes show significant variations. The Co-catalysed reaction is the most complex and the rate equation exhibits dependency on P_{CO}, methanol, Co and I^- concentrations. The mechanism is believed to parallel that of the Co-catalysed hydroformylation reaction, involving *neutral* rather than ionic species, with the addition of CH_3I (in place of olefin) to $HCo(CO)_x$ ($x = 3$ or 4) as the principal variant.[29] In contrast the rate equation for the Rh-catalysed reaction is remarkably simple, with first order dependences on [Rh] and $[CH_3I]$. Surprisingly, the rate is independent of the concentrations of both reactants and products; neither therefore, has any kinetic influence. A key intermediate in this system is known to be $[Rh(CO)_2I_2]^-$, which is the principal species present in solution under operating conditions, according to *in situ* infrared spectroscopic measurements, and the catalytic cycle involves only *anionic* Rh-containing species. The rate-determining step is the oxidative addition of methyl iodide to the Rh(I) anion to give a Rh(III) methyl complex which undergoes rapid migratory insertion with CO into the corresponding Rh(III) acetyl species.[28] The catalytic cycle operates as indicated in Fig. 3, which also emphasises the link between the separate organic and metal-catalysed components that are integrated into the complete process.

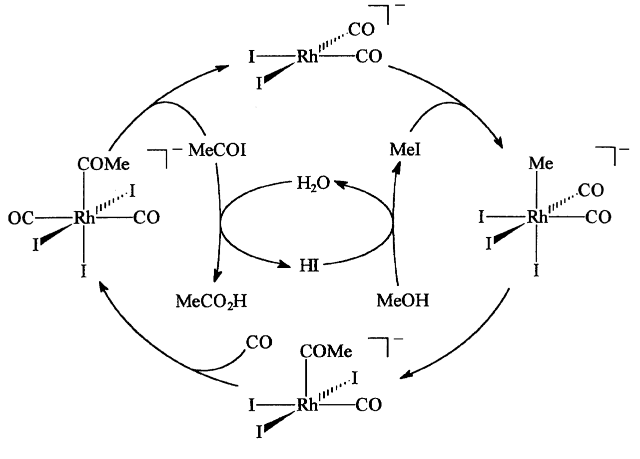

Fig. 3 Reaction mechanism for the Rh-catalysed carbonylation of methanol to acetic acid, showing the interlinked organic and metal catalysed components of the cycle.

Table 3 Comparison between Co-, Rh- and Ir-based methanol carbonylation processes

Operating parameters	Cobalt (BASF) (ref. 29)	Rhodium (Monsanto) (ref. 3)	Iridium (BP Chemicals) (ref. 4)
Pressure/bar	500–700	30–40	30–40
Temperature/°C	230	180	180
Metal concentration/M	*ca.* 10^{-1}	*ca.* 10^{-3}	*ca.* 10^{-3}
Promoter(s)	I^-	I^-	I^-, Ru complexes
Selectivity (%) based on methanol	*ca.* 90	99	99.5
By-products	Methane, acetaldehyde, ethanol, CO_2	Propionic acid, acetaldehyde condensation products	Neglible
Rate behaviour ∝	$[Co]^x[CH_3OH][I^-][P_{CO}]^2$ (x = variable)	$[Rh][I^-]$	$[Ir][P_{CO}][I^-]^{-1}$

Highly active iridium catalysts for methanol carbonylation have been known for many years and the initial chemistry was developed alongside that of Rh.[30] However, the catalytic chemistry is more complex than that of Rh, involving both *anionic* and *neutral* catalytic cycles; in addition, unproductive loss of CO *via* water gas shift chemistry (*via* the intermediacy of $[Ir(CO)_2I_4]^-$) was recognised as a significant problem.[31] The kinetic behaviour of the iodide-promoted Ir system[4] contrasts with that of both Co and Rh catalysts. The rate equation is first order in [Ir] and P_{CO} and inverse first order in $[I^-]$. Oxidative addition of CH_3I is extremely rapid and the subsequent migratory insertion reaction now becomes rate determining (Fig. 4), in direct contrast to the corresponding Rh chemistry.

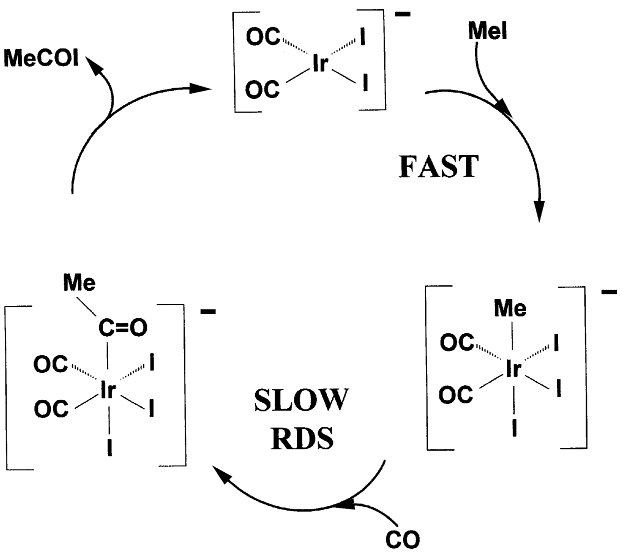

Fig. 4 Distinctive features of the Ir-catalysed carbonylation of methanol to acetic acid.

As a consequence, the resting state of the catalyst is $[CH_3Ir(CO)_2I_3]^-$ rather than $[Ir(CO)_2I_2]^-$, *cf.* Rh catalysts. From studies of model reactions, relative values of k_{Ir}/k_{Rh} for the oxidative addition and migratory insertion steps have been estimated as *ca.* 150 and 10^{-5}–10^{-6} respectively, and rationalised qualitatively in terms of the relative strengths of metal–carbon bonds in 4d and 5d transition metals.[32] The strength of a M–C bond to a 5d metal is generally higher than that to a corresponding 4d metal. As a consequence, if metal–ligand bond *making* plays a key role in a particular step, then the 5d metal is more likely to react faster (as in oxidative addition) whereas if a metal–ligand bond-*weakening* or -breaking step plays a key role in a process (as in migratory insertion), it is likely that the 4d metal will be the faster.

Another fundamental difference between Ir and Rh is that whereas high levels of CH_3I are required to give the highest reaction rates in Rh systems, with Ir the rate is largely independent of $[CH_3I]$. Also, the inverse dependence on ionic iodide concentration suggests that very high reaction rates should be attainable by operating at low total iodide concentrations. It also implies that the inclusion of a species capable of assisting iodide abstraction could enhance the new rate-limiting step. Metal carbonyl catalyst promoters containing Ru, Os, and Re have been found to be particularly effective in the latter respect.[4] In addition, they have been shown to act as CO donors, which results in the net effect of decreasing the P_{CO} dependency of the iodide-promoted system alone. Ruthenium co-promoters such as $Ru(CO)_4I_2$ have proven particularly effective in the commercial process but their mode of action has yet to be unequivocally defined.

Preliminary ^{13}C NMR spectroscopic results (jointly with Andrew P. Wright, Jonathan A. Iggo and Brian T. Heaton) on the speciation of ^{13}C-labelled Ru and Ir complexes, both separately and together (under carbon monoxide and/or dinitrogen) in CH_2Cl_2 or THF, in key model reactions that comprise likely components of the catalytic cycle are proving instructive. A plausible, internally-consistent working model on which to base the promotional effects of Ru complexes on the Ir-catalysed process is in the course of development.[33] The ^{13}C NMR spectroscopic parameters of several key intermediates, including $[CH_3Ir(CO)_2I_3]^-$, $CH_3Ir(CO)_3I_2$, $[(CH_3CO)Ir(CO)_2I_3]^-$, $Ru(CO)_4I_2$ and *fac*-$[Ru(CO)_3I_3]^-$ have been documented and their stereochemistries unambiguously assigned (see Table 4). It has also been found that HI competes more effectively than CH_3I for $[Ir(CO)_2I_2]^-$ with respect to the formation of the undesired oxidative addition products $[HIr(CO)_2I_3]^-$ and $[Ir(CO)_2I_4]^-$. An investigation of the interaction between $Ru(CO)_4I_2$ and $[CH_3Ir(CO)_2I_3]^-$ in solution, using ^{13}C NMR spectroscopy, has enabled the detection and characterisation of new iodide-bridged Ru–Ir and Ir–Ir dimers.

Role(s) of Ru in promotion of the Ir catalyst for methanol carbonylation

The principal role of Ru appears to be related to the promotion of an iodide abstraction process primarily *via* the following equilibrium:

$$Ru(CO)_4I_2 + I^- \rightleftharpoons [Ru(CO)_3I_3]^- + CO$$

This is manifested in two distinct aspects: the first as a competitive scavenger (relative to Ir) of any free HI formed in the hydrolysis step during the carbonylation catalysis. Ruthenium has been shown to compete more effectively than Ir for HI (but *not* CH_3I) *via* the above equilibrium with a consequent inhibition of the oxidative addition of HI to $[Ir(CO)_2I_2]^-$ and subsequent conversion into the undesired $[Ir(CO)_2I_4]^-$:

$$[Ir(CO)_2I_2]^- + HI \longrightarrow [HIr(CO)_2I_3]^-$$
$$[HIr(CO)_2I_3]^- + HI \longrightarrow [Ir(CO)_2I_4]^- + H_2$$

Initiation of the undesired and unproductive water gas shift chemistry associated with Ir catalysis in the presence of $[Ir(CO)_2I_4]^-$ (ref. 31) is therefore inhibited.

Table 4 Spectroscopic parameters for selected complexes identified in this work

Complex	^{13}C (ppm)	^{1}H (ppm)	J(C–H) and J(C–C)*/Hz	$\nu(^{12}CO)/cm^{-1}$
cis-$[Ir(CO)_2I_2]^-$	170.1, s	—	—	2046, 1970
$[CH_3Ir(CO)_2I_3]^-$	156.0, s; −16.2, q	2.1, d	139.4 (^1J)	2095, 2045
cis-$[Ir(CO)_2I_4]^-$	149.9	—	—	2111, 2067
$[HIr(CO)_2I_3]^-$	154.5, d	−11.6	2.7 (^2J)	2102, 2052
trans-$[(CH_3CO)Ir(CO)_2I_3]^-$	199.8, d; 161.1, s; 50.9, d	2.8	32.2 (^1J)*	
fac-$[Ru(CO)_3I_3]^-$	187.3, s			2097, 2027
$[I_2(CO)_3Ru–I–Ir(CH_3)(CO)_2I_2]^-$	187.1, t; 186.2, d; 155.3, s; −141, s		3.39 (^2J)*	

s = singlet, d = doublet, t = triplet, q = quartet.

The second role of Ru as an iodide abstractor has been revealed during monitoring (by ^{13}C NMR spectroscopy) of reactions in which $Ru(CO)_4I_2$ is added to solutions containing $[CH_3Ir(CO)_2I_3]^-$, the resting state of the catalyst, under a range of reaction conditions.[33] Under a dinitrogen atmosphere, careful spectral analysis as a function of time is consistent with the formation of an iodide-bridged Ru–Ir dimer that has been fully characterised in solution by ^{13}C NMR spectroscopy (Fig. 5). Under 6 bar CO this dimer is readily cleaved to give $[Ru(CO)_3I_3]^-$ (by iodide abstraction from Ir) with the co-formation of the *neutral* methyl–iridium complex CH_3-$Ir(CO)_3I_2$.

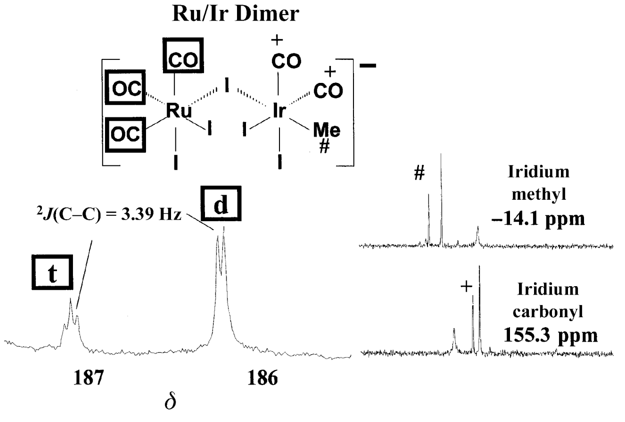

Fig. 5 ^{13}C NMR spectroscopic data for intermediate Ru–Ir dimer.

$$Ru(CO)_4I_2 + [CH_3Ir(CO)_2I_3]^- \longrightarrow [I_2(CO)_3Ru–I–Ir(CH_3)(CO)_2I_2]^- + CO$$

$$[I_2(CO)_3Ru–I–Ir(CH_3)(CO)_2I_2]^- + CO \longrightarrow [Ru(CO)_3I_3]^- + CH_3Ir(CO)_3I_2$$

In the presence of excess $[CH_3Ir(CO)_2I_3]^-$ the formation of an iodide-bridged Ir dimer has also been detected and characterised (together with the co-formation of $[Ru(CO)_3I_3]^-$) under di-nitrogen; this dimer also undergoes cleavage under 6 bar CO to give both the *neutral* $CH_3Ir(CO)_3I_2$ and anionic $[CH_3Ir(CO)_2I_3]^-$.

$$[I_2(CO)_3Ru–I–Ir(CH_3)(CO)_2I_2]^- + [CH_3Ir(CO)_2I_3]^- \xrightarrow{N_2} [Ru(CO)_3I_3]^- + [CH_3Ir(CO)_2I_2–I–Ir(CO)_2I_2(CH_3)]^-$$

$$[CH_3Ir(CO)_2I_2–I–Ir(CO)_2I_2(CH_3)]^- + CO \longrightarrow CH_3Ir(CO)_3I_2 + [CH_3Ir(CO)_2I_3]^-$$

The *neutral* species methyliridium tricarbonyl di-iodide is known to be considerably more active towards migratory insertion of CO (by a factor of *ca.* 800) than the *anionic* resting state of the catalyst $[CH_3Ir(CO)_2I_3]^-$; any enhancement of the concentration of the former in solution must therefore lead to an acceleration in the overall rate of carbonylation.[32]

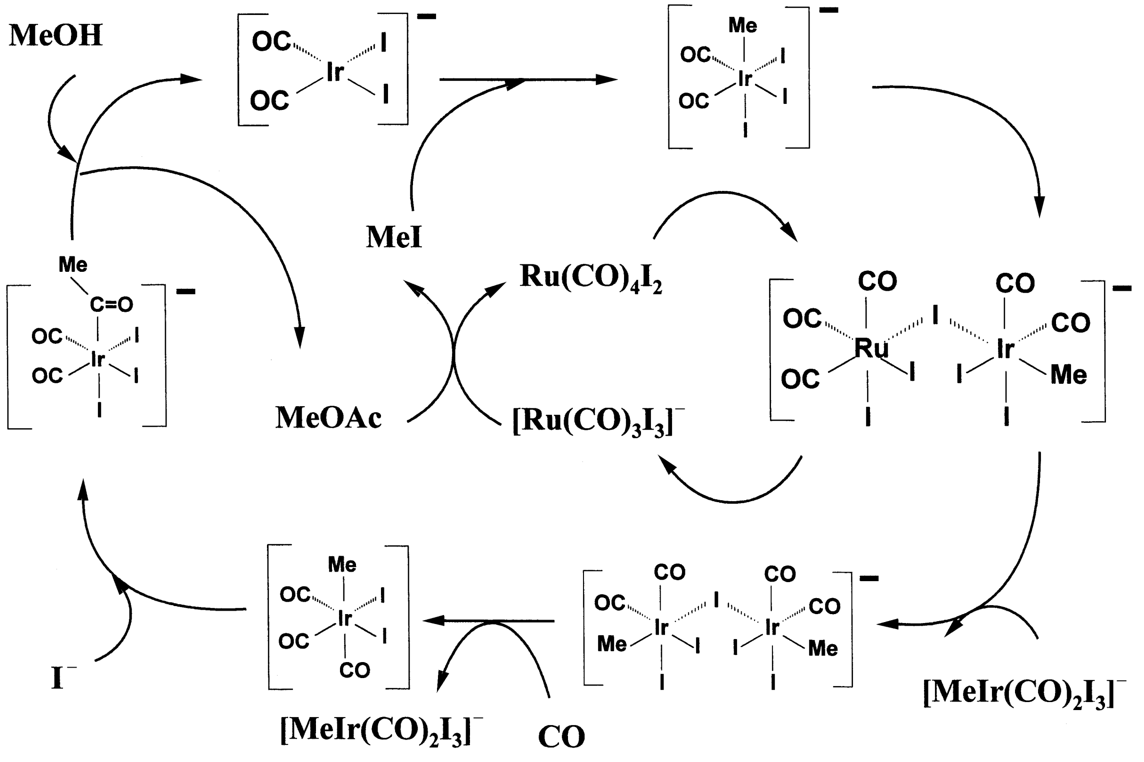

Fig. 6 Proposed reaction mechanism for the Ru-promoted, Ir-catalysed carbonylation of methanol to acetic acid.

In both examples the halogen abstraction process involves the formation of *fac*-$[Ru(CO)_3I_3]^-$, a species that has been shown previously to be of high thermodynamic stability,[8,34,35] and one that does not readily undergo reversal to $Ru(CO)_4I_2$ under CO in typical organic solvents such as CH_2Cl_2 and THF. In our most recent work we have however demonstrated the feasibility of a facile regeneration of $Ru(CO)_4I_2$ from $[Ru(CO)_3I_3]^-$ *via* reaction with CO in methyl acetate as solvent/reactant:

$$[Ru(CO)_3I_3]^- + CO + CH_3CO_2CH_3 \longrightarrow Ru(CO)_4I_2 + CH_3I + CH_3CO_2^-$$

In the mixed Ir–Ru system the methyl iodide co-product may then be readily scavenged in solution *via* rapid oxidative addition to $[Ir(CO)_2I_2]^-$, as discussed previously.

Consideration of the two aspects of iodide abstraction by $Ru(CO)_4I_2$, together with the demonstration of its regeneration *via* the above reaction, has allowed the catalytic cycle in Fig. 6 to be proposed. The effective role of the Ru co-promoter can thus be summarised as (i) competitive removal of HI to prevent entry into a rate-limiting Ir-catalysed water gas shift cycle and (ii) abstraction of iodide from the anionic resting state of the Ir catalyst to facilitate formation of the neutral $CH_3Ir(CO)_3I_2$ which is considerably more susceptible than its anionic analogue $[CH_3Ir(CO)_2I_3]^-$ towards migratory CO insertion and acyl formation.

Conclusion

It is anticipated that this contribution to Dalton Discussion 4 will both enhance the general awareness, and stimulate interest, within the reaction mechanisms community, concerning the potential inherent in the derivation of improved mechanistic understanding of the effects of catalytic promoters in homogeneously catalysed reactions, particularly in relation to the activation of carbon monoxide.

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