Analysis of the Synergistic Effect of Carbonylplatinum Complexes on the Iridium-Catalysed Carbonylation of Methanol to Acetic Acid

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High-pressure NMR mechanistic investigations into the promoting role of dicarbonyldiiodoplatinum complex in the iridium-catalysed carbonylation of methanol to acetic acid are consistent with iodide abstraction from the [IrI₃(CH₃)(CO)₂]⁻ resting state species by [PtI₂(CO)₂], unbolting the rate-limiting migratory CO insertion step. A new [Ir-Pt] heterodimetal-

Introduction

Carbonylation of methanol is the major route to the production of acetic acid, and the worldwide industrial manufacture associated with this homogeneous catalytic process reaches 6.10⁶ tons/year [Equation (1)]. This reaction involves a complex mixture of reactants consisting of water, acetic acid, methyl iodide, methyl acetate, hydroiodic acid, and traces of propionic acid, from which methanol is absent as it is immediately converted by HI into CH₃I. Many efforts have been aimed at the substitution of iridium for rhodium since the former tolerates low levels of water during the reaction, saving operating costs in the separation step of water from acetic acid.

$$CH_3OH + CO \xrightarrow{Cat} CH_3COOH$$
 (1)

Moreover, in the active species $H[IrI_2(CO)_2](1)$ the metal centre is more nucleophilic than that in the homologous rhodium precursor used in the Monsanto process,^[1] so that the rate of the first step of the catalytic cycle, the oxidative

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lic complex, which presumably represents the key species involved in the abstraction of I-, has been characterised by NMR in tandem with FAB-MS.

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addition of CH_3I affording $[IrI_3(CH_3)(CO)_2]^-$ (2), is largely enhanced.^[2] The subsequent step, the migratory CO insertion leading to an Ir-acetyl species is so slow^[3] that a process based on iridium cannot be suitable for industrial applications. In 1994, Watson et al. discovered that addition of ruthenium promoters to the iridium catalyst resulted in a dramatic increase in catalytic activity,^[4] and very recent reports^[5,6] have shown that this is due to the abstraction of an iodo ligand from 2, allowing the rapid migratory insertion of CO into the Ir-CH₃ bond. The authors have proposed an intermediate [Ir-Ru] heterodimetallic complex, which has not been detected. In 1998, we patented the promoting effect of platinum,^[7] which gives performances comparable to the iridium/ruthenium system in terms of turnover frequencies (2500 h⁻¹ for Ir-Pt and 2800 h⁻¹ for Ir-Ru, respectively, expressed with regard to Ir). For the two dimetallic systems, maximum activities are found for water concentrations close to 5 wt.-%, whereas the corresponding value approaches 14 wt.-% for the Monsanto process.

We envisaged that in both cases the catalytic cycles could present some common features. Thus, we undertook investigations on the [Ir-Pt] system in order to obtain a deeper insight into the nature of the intermediates that are formed and are responsible for the iodide abstraction from 2. At first, we decided to study the catalytic complex mixtures by high-pressure NMR spectroscopy under conditions that closely resemble those used in the industrial process. Relevant pieces of information arise from the use of ¹³C-enriched reactants, such as ¹³CO, ¹³CH₃¹³COO¹³CH₃, and ¹³CH₃I in ¹³C and ¹⁹⁵Pt NMR spectroscopy. Thus, we were able to focus on every part of the catalytic cycle, using a procedure that leads to the detection of the transition metal complexes bearing carbonyl and methyl or acyl ligands. We



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present here our first mechanistic results based on highpressure NMR (13 C, 1 H, 195 Pt) experiments. Moreover, in order to characterise the short-lived complexes involved in this process, we used the bis(triphenylphosphoranylidene) [PPN]⁺ stabilising counterion and made observations at room temperature by NMR in tandem with FAB-MS. The new heterodimetallic species [IrI(CH₃)(CO)₂(µ-I)₂PtI₂(CO)]⁻ has been identified and its evolution monitored in solution.

The iridium complex 1 alone, initially studied by Forster^[2] and Pannetier et al.,^[8] is known to slowly catalyse the carbonylation of methanol to acetic acid. In mixtures similar to those employed industrially,^[9] under 3 MPa and at 95 °C, we observed by high-pressure ¹³C NMR spectroscopy (100.6 MHz) the spontaneous formation of the methyliridium complex H[Ir(${}^{13}CH_3$)I₃(${}^{13}CO$)₂] (**2**) together with small amounts of the acyl species H[Ir(${}^{13}CO{}^{13}CH_3$)-I₃(${}^{13}CO$)₂] (**4**) (see Table 1). As previously proposed by Forster from IR observations,^[2] we confirm that under these conditions the resting state is the methyl complex **2**, which is characterised by signals at $\delta = 157.1$ (s, CO), -15.2 [q, ${}^{1}J(C,H) = 141$ Hz, CH₃] ppm. These NMR values are very close to those for [PPN][Ir(CH₃)I₃(CO)₂], which was characterised by X-ray crystallography.^[10] Small amounts of CO₂ were also detected, resulting from the water gas shift side reaction (WGSR). In addition, some CH₄ was detected. Evidence of occurrence of the WGSR was provided by the presence of H[IrHI₃(CO)₂] and H[IrI₄(CO)₂], as shown by the relevant NMR spectroscopic data. The low activity of **2** was also shown by the low consumption of ${}^{13}CO$ and

Table 1. NM	R spectrosco	pic data for	the species	involved in	the methanol	carbonvlation 1	eaction.

Complex	¹³ C NMR (δ/ppm)	Products	¹³ C NMR (δ/ppm)
$PPN[IrI_2(CO)_2] (1)$	169.9 (s, CO)	AcOH	177.3 (s), 21.1 (q)
$H[IrHI_3(CO)_2]$	156.0 (s, CO)	AcOMe	172 (s), 52 (q), 21 (q)
$H[IrI_4(CO)_2]$	151.3 (s, CO)	MeI	-25.0 (q)
$H[IrI_3Me(CO)_2]$ (2)	157.1 (s, CO), -15.2 (q, $J_{C,H} = 141$ Hz, CH ₃)	MeOH	49.3 (q)
$[IrI_2Me(CO)_3]$ (3)	146.9 (s, CO), -22.3 (q, $J_{C,H} = 140$ Hz, CH ₃)	CO_2	125 (s)
$H[IrI_3(COMe)(CO)_2]$ (4)	203.4 (s, COMe), 160.7 (s, CO), 50.6 (q, $J_{C,H}$ = 140 Hz, CH ₃)	CO	185.4 (s)
H[PtI ₃ (CO)] (6) [PtI ₂ (CO) ₂] (5)	156.8 (s, d, J_{Pt-C} = 1649 Hz, CO) 154.5 (s, d, J_{Pt-C} = 1843 Hz, CO)	CH_4	-4.2 (quint)



Figure 1. High-pressure ¹³C NMR of the [Ir] system (a) and the [Pt-Ir] system (b).

¹³CH₃I.^[11] Thus, in the absence of any stabilising counterion, we have established the nature of the catalytic species that present the longest life-times.

Subsequently, our studies focused on the accelerating effect of platinum promoters on the iridium system. Under 3 MPa (${}^{13}CO/{}^{12}CO = 1:3$) and at 95 °C in a high-pressure NMR sapphire tube, addition to the catalytic iridium mixture of [PtI₂(CO)₂] (**5**), which is the stable species formed

from $[Pt_2I_2(\mu-I)_2(CO)_2]$ under CO, led to a significant increase in the carbonylation rate. In batch experiments using a Hastelloy[®] reactor, we obtained a carbonylation rate (based on the transformation of AcOMe into acetic acid) of 16 molL⁻¹h⁻¹ with iridium alone, compared to 35 molL⁻¹h⁻¹ after addition of $[PtI_2(CO)]_2$ (Pt/Ir = 3:7). ¹³C NMR spectra led to observe the change in the concentration of the organic compounds during the catalytic runs



Figure 2. ¹³C NMR spectroscopic data for the [Ir-Pt]/methanol carbonylation system.



Figure 3. Proposed catalytic cycle for the [Ir-Pt] system.

and particularly the intensity ratio between the signals of acetic acid and methyl iodide. We have charged two highpressure NMR tubes with $IrI_{3.4}$, ¹³CH₃I (10 wt.-%), AcOMe (20 wt.-%), H₂O (6 wt.-%) and AcOH (64 wt.-%) under 30 bar of a mixture of $^{13}CO/^{12}CO$, one tube containing only $IrI_{3.4}$ salt (a) and the other containing the mixture of $IrI_{3.4}$ and $[PtI_2(CO)]_2$ (b). After 3 h at 86 °C, we can compare (Figure 1) the relative intensity ratios of the two signals of $^{13}CH_3I/AcOH$ and conclude that a larger amount (around two times) of $^{13}CH_3I$ was consumed^[11] with the [Ir–Pt] system than with the iridium catalyst only. Under these conditions, we observed the presence of H[PtI_3(CO)] (6) and the signals corresponding to the iridium complexes 2 and 4 in significant amounts^[12] (Figure 2).

The role of platinum is mainly to assist the formation of the species $[IrI_2(CH_3)(CO)_3]$ (3), in which the electron density on the iridium atom is reduced; migratory CO insertion can then occur more rapidly to produce 4. In separate experiments we checked that platinum indeed acts as a real co-catalyst, since application of 3 MPa of CO exerted on 6 provides 5 again, whereas such a platinum species alone does not catalyse the carbonylation reaction. Finally, reductive elimination of acyl iodide from 4 regenerates 1 (Figure 3).

In order to obtain a clear view of this dimetallic process, we decided to decrease the reaction rate by performing the experiments under ambient conditions and by using the [PPN]⁺ stabilising counterion under nitrogen. A number of ¹H NMR (250 MHz, CD₂Cl₂, 25 °C) spectra were recorded while varying the Ir/Pt molar ratio. Addition of $[Pt_2I_2(\mu-I)_2-$ (CO)₂] to a dichloromethane solution of 2-PPN provided several signals at $\delta = 2.36, 2.28, 2.14, 2.09, 1.90$ and 1.85 ppm (Figure 4). At low platinum concentrations (Ir/Pt = 9.5:1), the signal at δ = 2.14 ppm is assigned to unreacted **2-PPN**. We may tentatively assign the peak at $\delta = 2.09$ ppm to the solvated neutral species [IrI₂(CH₃)(CO)₂(solv)], in which the coordinated solvent could be CD₂Cl₂. Indeed, iridium(III) complexes containing coordinated CH₂Cl₂ have been reported previously.^[13] At higher platinum concentrations (Ir/Pt = 5.3:1), significant amounts of the two isomers of $[Ir_2I_2(\mu-I)_2(CH_3)_2(CO)_4]$ were detected at $\delta = 1.90$ and 1.85 ppm.^[10]



Figure 4. Detection of $[IrI(CH_3)(CO)_2(\mu-I)_2PtI_2(CO)]^-$ and $[Ir_2I_4(\mu-I)(CH_3)_2(CO)_4]^-$ by tandem NMR and FAB/MS experiments: top (Ir/Pt = 9.5:1), bottom (Ir/Pt = 5.3:1).



Scheme 1. Reaction route leading to Ir_2 -bridged species through the intermediate formation of an [Ir-Pt] dimetallic moiety (from 2 and $[Pt_2I_2(\mu-I)_2(CO)_2]$).

As already stated, two additional ¹H NMR signals appeared at δ = 2.36 and 2.28 ppm, whose relative intensities vary with the Ir/Pt molar ratio. In order to assign these two signals, for the given Ir/Pt ratios, we recorded ¹H NMR spectra in tandem (analysed from the same sample) with FAB/MS experiments. Representative examples are shown in Figure 4. For an Ir/Pt = 5.3:1 molar ratio, two anionic complexes were detected at m/z = 1121 and 1161. The former molecular peak corresponds to the anionic heterodimetallic complex $[IrI(CH_3)(CO)_2(\mu-I)_2PtI_2(CO)]^-$. The latter is consistent with the formulation $[Ir_2I_4(\mu-I)(CH_3)_2(CO)_4]^-$, which was previously suggested as an intermediate in the [Ir-Ru] system.^[5] In a second representative run, for an Ir/ Pt = 9.5:1 molar ratio, the peak at m/z = 1121 in the FAB/ MS spectra, as well as the signal at $\delta = 2.36$ ppm in the ¹H NMR spectra disappeared nearly completely. Thus, the signal at $\delta = 2.28$ ppm can be unambiguously assigned to the complex $[Ir_2I_4(\mu-I)(CH_3)_2(CO)_4]^-$. Additionally, ¹³C NMR spectra reveal the signals of $[Ir_2I_4(\mu-I)(CH_3)_2(CO)_4]^{-1}$ at δ = 154.68 ppm (s, CO), -14.83 ppm (q, $J_{C,H}$ = 141 Hz, CH₃) and two new carbonyl signals that correspond to $[IrI(CH_3)(CO)_2(\mu-I)_2PtI_2(CO)]^-$. The CO ligand coordinated to Pt gives a signal at $\delta = 154.9$ ppm (s, CO) with its satellites characterised by a doublet (${}^{1}J_{Pt,C} = 1650$ Hz, CO). The other carbonyl signal at $\delta = 155.4$ ppm (no coupling constant) is assigned to the two CO ligands coordinated to the iridium atom. The quadruplet at $\delta = -14.2$ (q, ${}^{1}J_{C,H} =$ 141 Hz, CH₃) ppm shows no coupling between ¹³C and ¹⁹⁵Pt and is presumably due to the CH₃ ligand coordinated to the iridium atom. The ¹⁹⁵Pt NMR spectra show a new signal at $\delta = -5462$ (s, + satellites d, ${}^{1}J_{\text{Pt,C}} = 1650$ Hz, CO) ppm, together with a signal of $[PtI_3(CO)]^-$ at $\delta = -5460$ (s, + satellites d, ${}^{1}J_{Pt,C}$ = 1759 Hz, CO) ppm. Scheme 1 summarises the reaction pathway for the formation and the evolution of the mixed [Ir-Pt] complex. Under CO, the [Ir-Pt] system leads very quickly to the two complexes 3 and 6.

This work presents circumstantial evidence that the main role of the platinum promoter during the iridium-catalysed carbonylation of methanol is to abstract an iodo ligand from $[IrI_3(CH_3)(CO)_2]^-$ (2) through the formation of the heterodimetallic $[IrI(CH_3)(CO)_2(\mu-I)_2PtI_2(CO)]^-$ intermediate species.

Experimental Section

Synthesis of the Iridium Complexes: The synthesis of the iridium complexes has been previously reported.^[10]

Synthesis of the Platinum Complexes

[PtI₂(CO)₂] (5) and [PtI₂(CO)]₂ (5'): [Pt(CO)₂I₂] was prepared by addition of PtI₂ (2 g, 4.45 mmol) in an autoclave containing hexane (125 mL). The mixture was pressurised with CO (12 bar) and stirred at 75 °C for 1 h. The solution was cooled in the reactor under CO (1 bar). 1.69 g (80% yield) of a red solid was obtained and dried under reduced pressure, which corresponds to [PtI₂(CO)]₂. Under CO, this compound leads to [PtI₂(CO)₂] in 100% yield. [PtI₂(CO)]₂: IR (CH₂Cl₂): $\tilde{v} = 2111$ (CO) cm⁻¹. ¹³C NMR (CD₂Cl₂): $\delta = 154.5$ (s, ¹*J*_{Pt-C} = 1843 Hz, CO) ppm. ¹⁹⁵Pt NMR (CD₂Cl₂): $\tilde{v} = 2127$ (CO) cm⁻¹. ¹³C NMR (CD₂Cl₂): $\delta = 166$ (s, ¹*J*_{Pt-C} = 1466 Hz, CO) ppm. ¹⁹⁵Pt NMR (CD₂Cl₂): $\delta = -5790$ (¹*J*_{Pt-C} = 1466 Hz) ppm.

[PPN][PtI₃(CO)] (6-PPN): [PtI₂(CO)]₂ (1 g, 1.05 mmol) was dissolved in dichloromethane (50 mL), and HI (0.26 g, 2.10 mmol) was added to give rapidly, at room temperature, the complex H[PtI₃(CO)]. Then, [PPN]Cl (1.20 g, 2.10 mmol) was added to the solution. The solvent was removed under vacuum to give a yellow product. Crystallisation of this compound in CH₂Cl₂/hexane (1:1) gave yellow crystals of [PPN][PtI₃(CO)] (1.08 g, 45%). IR (CH₂Cl₂): $\tilde{v} = 2075$ (CO) cm⁻¹. ¹³C NMR (CD₂Cl₂): $\delta = 152.8$ (s, ¹*J*_{Pt-C} = 1759 Hz, CO) ppm. ¹⁹⁵Pt NMR (CD₂Cl₂): $\delta = -5460$ (¹*J*_{Pt-C} = 1759 Hz). MS (FAB⁻): *m*/*z* = 603.

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- $\begin{array}{ll} [9] & IrI_3, IrI_4 \ (0.05 \ mol), \ AcOH \ (64 \ wt.-\%), \ H_2O \ (6 \ wt.-\%), \ AcOMe \ (20 \ wt.-\%), \ ^{13}CH_3I \ (10 \ wt.-\%). \end{array}$

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