

A highly efficient catalyst precursor for ethanoic acid production: [RhCl(CO)(PEt₃)₂]; X-ray crystal and molecular structure of carbonyldiido(methyl)bis(triethylphosphine)rhodium(III)

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Under mild conditions, [RhI(CO)(PEt₃)₂], is more active for the carbonylation of methanol to ethanoic acid than [Rh(CO)₂I₂]⁻, which is widely used industrially; intermediates in the catalytic cycle have been identified and characterised.

The [Rh(CO)₂I₂]⁻ catalysed carbonylation of methanol is the most widely used commercial route to ethanoic acid.¹ The rate determining step for the catalytic cycle² is oxidative addition of iodomethane to [Rh(CO)₂I₂]⁻, so that increasing the electron density on the metal centre should increase the rate of oxidative addition and hence the overall rate of production of ethanoic acid. There have been attempts to modify [Rh(CO)₂I₂]⁻ by using electron donating ligands.^{3–6} For instance, Baker *et al.*³ used [RhI(CO)(Ph₂PCH₂P(S)Ph₂)] to enhance the rate of carbonylation at 185 °C. Cavell and coworkers⁴ prepared complexes of the form, [RhCl(CO)(PPh₂CH₂PPh₂NR)], where R is a substituted phenyl group. Wegman *et al.*⁵ compared the methanol carbonylation rate at 80 °C using [Rh(CO)₂I₂]⁻ and [RhCl(CO)₂(Ph₂P(CH₂)₂P(O)Ph₂)] and noted an 80-fold increase with the latter. Dilworth *et al.*⁶ used rhodium(I) carbonyl complexes containing phosphinothiolate and thioether ligands to promote the rate of carbonylation of methanol under the relatively forcing conditions of 70 bar and 185 °C. To our knowledge, the use of trialkylphosphines as promoters for rhodium based carbonylation catalysts has not been investigated, despite the fact that they are strongly electron donating. We now report the results of such a study.

Complexes of the form [RhX(CO)(PEt₃)₂] (X = Cl, Br or I) have ν_{CO} at *ca.* 1960 cm⁻¹ compared with 1988 and 2059 cm⁻¹ for [Rh(CO)₂I₂]⁻, suggesting that the rhodium centre is more electron rich in the triethylphosphine complexes. We have shown that these complexes are active for the double carbonylation of CH₂I₂⁷ and of allylic halides⁸ and so have attempted to increase the rate of carbonylation of methanol by using these complexes and have found that [RhCl(CO)(PEt₃)₂] is an extremely active catalyst precursor for ethanoic acid production. We report the first direct comparison of [Rh(CO)₂I₂]⁻ with a rhodium phosphine complex under the conditions of 120–150 °C and 27 bar carbon monoxide pressure. The initial carbonylation rates using [RhCl(CO)(PEt₃)₂] and [Rh(CO)₂Cl]₂ as sources of rhodium at 120 and 150 °C in the presence of differing water concentrations are shown in Table 1.

The results of Table 1 show that, in the presence of 17.1% m/m H₂O under the mild conditions of 120 or 150 °C and 27 bar pressure (runs 1–4), [RhI(CO)(PEt₃)₂] catalyses the carbonylation of methanol at a rate nearly double that of [Rh(CO)₂I₂]⁻. Water acts to maintain the catalyst in its active form⁹ *i.e.* as a rhodium(I) complex and decreases the formation of inactive rhodium(III) complexes such as [Rh(CO)₂I₄]⁻ or [RhI₃(CO)(PEt₃)₂]. Thus, as shown in Table 1, the rate of carbonylation is dramatically enhanced in the presence of a significant concentration of water. Under lower water conditions (runs 5 and 6), no appreciable benefit is obtained by using [RhCl(CO)(PEt₃)₂] over [Rh(CO)₂Cl]₂ as catalyst precursors.

The mechanistic cycle has been studied using high pressure and variable temperature NMR and high pressure IR spectroscopies¹⁰ as well as stoichiometric reactions. Thus, addition of methyl iodide to [RhI(CO)(PEt₃)₂] in CH₂Cl₂ leads smoothly to the formation of [RhMeI₂(CO)(PEt₃)₂], which has been fully characterised spectroscopically[‡] and by single crystal X-ray diffraction§ (Fig. 1). The methyl group is *cis* to the carbon monoxide, as required for migratory insertion. There have been no previously published crystallographic analyses of complexes of the type [RhX₂Me(CO)(PR₃)₂]. However, there are examples of crystal structures of other six-coordinate rhodium phosphine complexes where methyl iodide has been oxidatively added.^{11–13} Most have iodide and methyl ligands in mutually *trans* positions.

The isolation of the methyl complex for a catalytically active system is rather unusual since, generally, the insertion of carbon monoxide into the Rh–C bond is extremely rapid. For [Rh(CO)₂I₂]⁻, the methyl complex has a very short lifetime and has only been detected as a transient by IR spectroscopy in neat methyl iodide,¹⁴ whilst for the related [RhCl(CO)(PPh₃)₂], oxidative addition of methyl iodide gives the six-coordinate [RhMeClI(CO)(PPh₃)₂], but this is in equilibrium with the five-coordinate insertion product, [RhClI(MeCO)(PPh₃)₂].¹⁵ Presumably the high electron density on the metal in [RhMeI₂(CO)(PEt₃)₂] is responsible for the less facile methyl migration in this case. Despite the stability of the methylrhodium(III) complex, preliminary kinetic studies suggest that oxidative addition of MeI is still rate determining. The catalytic reaction

Table 1 Results of carbonylation experiments^a

Run	T/°C	Rhodium source	Initial water (% m/m)	Initial rate/mol dm ⁻³ h ⁻¹
1	120	[RhCl(CO)(PEt ₃) ₂] ^b	17.1	1.6
2	120	[Rh(CO) ₂ Cl] ₂ ^c	17.1	0.9
3	150	[RhCl(CO)(PEt ₃) ₂] ^b	17.1	9.2
4	150	[Rh(CO) ₂ Cl] ₂ ^c	17.1	5.0
5	120	[RhCl(CO)(PEt ₃) ₂] ^b	3.2	0.6
6	120	[Rh(CO) ₂ Cl] ₂ ^c	3.2	0.6

^a Experiments were carried out in a 300 cm³ Hastelloy B2 autoclave equipped with a ballast vessel, MagneDrive stirrer, liquid injection facility and cooling coils. For reactions requiring 17.1% H₂O m/m, a solution of MeCOOH (987 mmol), MeOAc (474 mmol), H₂O (1.82 mol) and MeI (396 mmol) was charged to the vessel. Similarly for reactions requiring 3.2% H₂O m/m, a solution of MeCOOH (1.75 mol), MeOAc (286 mmol), H₂O (354 mmol) and MeI (396 mmol) was charged to the vessel. The reaction vessel was heated to the required temperature whilst stirring under *ca.* 5 bar CO pressure. Once the desired temperature had been reached, the rhodium source, dissolved in MeOAc (13.5 mmol) and MeCO₂H (117 mmol), was injected into the autoclave to initiate the reaction. The autoclave was pressurised to 27 bar and stirred at 600 rpm. The rate of carbonylation was monitored by recording the rate of carbon monoxide uptake from a ballast vessel every 2 s. ^b Assumed to form [RhI(CO)(PEt₃)₂] rapidly under the reaction conditions. ^c Forms [Rh(CO)₂I₂]⁻ under the reaction conditions.

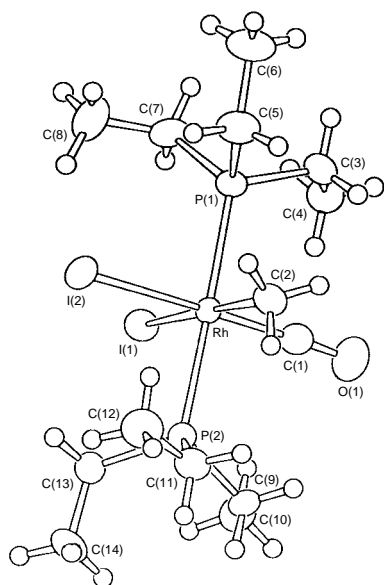


Fig. 1 X-Ray crystal structure and numbering scheme for $[\text{RhMeI}_2(\text{CO})(\text{PEt}_3)_2]$

is zero order in p_{CO} and first order in $[\text{MeI}]$. However, we have found that at 298 K the rate of oxidative addition of MeI for $[\text{RhI}(\text{CO})(\text{PEt}_3)_2]$ ($1.37 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) is 57 times faster than that for $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ ($2.39 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$); this compares with 120 times faster¹⁶ for $[\text{Ir}(\text{CO})_2\text{I}_2]^-$ relative to $[\text{Rh}(\text{CO})_2\text{I}_2]^-$.

Migratory insertion of carbon monoxide occurs under CO pressure (27 bar) to form $[\text{RhI}_2(\text{MeCO})(\text{CO})(\text{PEt}_3)_2]$ which has been fully spectroscopically characterised.[‡] The rate of the insertion reaction at room temperature and 27 bar is 38 times slower than for $[\text{RhMe}(\text{CO})_2\text{I}_3]^-$,[¶] but this slowing is not sufficient to make the migratory insertion step rate determining at 150 °C (shifts to 1740 cm^{-1} , MeOAc, on addition of MeOH). In contrast, for $[\text{Ir}(\text{CO})_2\text{I}_2]^-$, the insertion reaction is slowed by 10^5 – 10^6 times¹⁶ compared to $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ and becomes rate determining.

Heating a solution of $[\text{RhI}_2(\text{MeCO})(\text{CO})(\text{PEt}_3)_2]$ to 75 °C in the presence of excess methyl iodide and 40 bar carbon monoxide produces a product with a large absorption at 1799 cm^{-1} arising from ethanoyl iodide.¹⁷ This reductive elimination step completes the catalytic cycle. It has been shown that the usual mechanism for the formation of ethanoic acid or methyl ethanoate involves reductive elimination of ethanoyl iodide followed by reaction with water or methanol;^{2,18} however, it is unusual to observe ethanoyl iodide. The high electron density on the rhodium centre caused by the electron donating system would be expected to favour the Rh^{I} complex, $[\text{RhI}_2(\text{MeCO})(\text{CO})(\text{PEt}_3)_2]$, over $[\text{RhI}(\text{CO})(\text{PEt}_3)_2]$ and MeCOI. However, the way in which the reaction is performed allows the catalytic production of MeCOI because the Rh^{I} complex can be trapped by addition of methyl iodide when this is in excess. The overall catalytic cycle for the carbonylation of methanol in the presence of $[\text{RhI}(\text{CO})(\text{PEt}_3)_2]$, for which each complex has been characterised, is shown in Scheme 1.

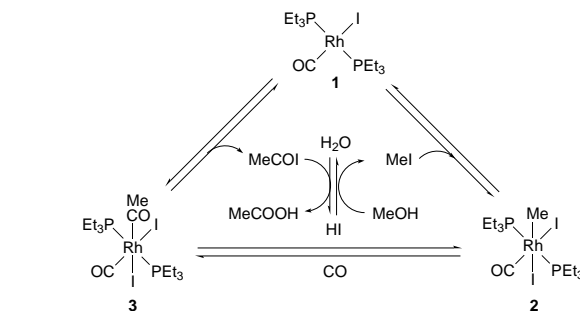
At 150 °C the catalyst loses activity over ca. 10 min with the formation of Et_3PO and $[\text{Rh}(\text{CO})_2\text{I}_2]^-$. Current studies are aimed at stabilising the catalyst towards phosphine loss.

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Footnotes and References

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Scheme 1 Proposed cycle for the carbonylation of methanol catalysed by $[\text{RhI}(\text{CO})(\text{PEt}_3)_2]$

‡ Selected spectroscopic data: all NMR spectra were recorded in CD_2Cl_2 unless otherwise stated. For **1**: $^31\text{P}\{^1\text{H}\}$: δ 20.2 (d, $^1J_{\text{RhP}}$ 111 Hz); $^{13}\text{C}\{^1\text{H}\}$: δ (CO) 186.0 (dt, $^1J_{\text{RhC}}$ 79 Hz, $^2J_{\text{PC}}$ 16 Hz); $\nu_{\text{CO}}/\text{cm}^{-1}$ (CH_2Cl_2) 1961. For **2**: $^31\text{P}\{^1\text{H}\}$: δ 2.4 (d, $^1J_{\text{RhP}}$ 85 Hz); $^{13}\text{C}\{^1\text{H}\}$: δ (CO) 183.3 (dt, $^1J_{\text{RhC}}$ 64 Hz, $^2J_{\text{PC}}$ 10 Hz), δ (CH_3) -3.1 (dt, $^1J_{\text{RhC}}$ 19 Hz, $^2J_{\text{PC}}$ 4 Hz); $\nu_{\text{CO}}/\text{cm}^{-1}$ (CH_2Cl_2) 2043. For **3**: $^31\text{P}\{^1\text{H}\}$: δ 2.1 (d, $^1J_{\text{RhP}}$ 88 Hz); $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6): δ (CO) 179.3 (dt, $^1J_{\text{RhC}}$ 69 Hz, $^2J_{\text{PC}}$ 8 Hz), δ (COCH_3) 226 (dt, $^1J_{\text{RhC}}$ 25 Hz, $^2J_{\text{PC}}$ 5 Hz), δ (COCH_3) 47.6 (d, $^2J_{\text{RhC}}$ 3 Hz); $\nu_{\text{CO}}/\text{cm}^{-1}$ (CH_2Cl_2) 2065, 1665.

§ Crystal data for **2**, $[\text{RhMeI}_2(\text{CO})(\text{PEt}_3)_2]$, $\text{C}_{14}\text{H}_{33}\text{I}_2\text{OP}_2\text{Rh}$, $M_r = 636.08$, monoclinic, space group Pn (no. 7), $a = 7.402(5)$, $b = 11.785(5)$, $c = 12.520(4)$ Å, $\beta = 96.01(4)^\circ$, $U = 1086.2(9)$ Å³, $Z = 2$, $D_c = 1.95 \text{ g cm}^{-3}$, $F(000) = 612$, $\mu(\text{Mo-K}\alpha) = 37.7 \text{ cm}^{-1}$, $\lambda = 0.71069$ Å, $T = 220$ K. Crystal size, $0.5 \times 0.4 \times 0.4$ mm. Of the 2787 reflections which were collected ($3 < 2\theta < 50^\circ$) on a Rigaku AFC7S diffractometer, 2598 were unique and 2453 were observed. Structure solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The maximum and minimum residual electron densities are 1.29 and -1.19 e \AA^{-3} . $R = 0.026$, $R_w = 0.027$. CCDC 182/566.

Important dimensions: bond lengths (Å): Rh–P(1) 2.387(2), Rh–P(2) 2.390(2), Rh–C(1) 1.836(9), Rh–C(2) 2.109(9), Rh–I(1) 2.7823(7), Rh–I(2) 2.721(1), C(1)–O(1) 1.113(10); bond angles ($^\circ$) I(1)–Rh–I(2) 94.18(4), I(1)–Rh–P(2) 91.36(5), I(1)–Rh–C(2) 173.8(2), I(2)–Rh–P(2) 88.22(5), I(2)–Rh–C(2) 91.8(2), P(1)–Rh–C(1) 92.2(3), P(2)–Rh–C(1) 90.0(3), C(1)–Rh–C(2), 85.0(3), I(1)–Rh–P(1) 90.34(5), I(1)–Rh–C(1) 89.0(2), I(2)–Rh–P(1) 89.48(5), I(2)–Rh–C(1) 176.3(2), P(1)–Rh–P(2) 177.24(7), P(1)–Rh–C(2) 88.1(2), P(2)–Rh–C(2) 90.4(2).

¶ For $[\text{RhMe}(\text{CO})_2\text{I}_3]^-$ this insertion reaction is independent of carbon monoxide pressure whilst for $[\text{RhMeI}_2(\text{CO})(\text{PEt}_3)_2]$ a first order dependence on carbon monoxide is observed.

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