High activity cobalt based catalysts for the carbonylation of methanol

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[Cp*Co(CO)$_2$] in the presence of PEt$_3$ and MeI catalyses the carbonylation of methanol with initial rates up to 44 mol dm^{-3} h^{-1} before decaying to a second catalytic phase with rates of 3 mol dm^{-3} h^{-1}; [CoI(CO)$_2$(PEt$_3$)$_2$], which is trigonal bipyramidal with axial PEt$_3$ ligands, has been isolated from the final reaction solution.

Ethanoic acid is a bulk chemical of major importance in the polymer, paints and other industries. It is currently mainly manufactured by the carbonylation of methanol in the presence of iodomethane.[1] The first process of this kind used [Co$_2$(CO)$_8$] as the catalyst precursor, but the low activity and selectivity of this system meant that high temperatures and pressures (200 °C, 600 bar) were required and the selectivity to methanol was low.[2]

The discovery that rhodium[3] or iridium[4] based catalysts operate more selectively under much milder conditions (180 °C, 30 bar) led to these processes becoming favoured commercially. However, because of the much lower cost of cobalt than of its two platinum group metal congeners, there would be considerable interest if cobalt based systems that operated with high activity and selectivity under mild conditions could be discovered. In this paper, we report evidence that cobalt based systems can display very high activity and high selectivity.

Fig. 1 shows plots of gas (CO) uptake from a ballast vessel attached to an autoclave at constant pressure by solutions of [Cp*Co(CO)$_2$] under various conditions. [Cp*Co(CO)$_2$] in methanol containing methyl iodide shows relatively low activity but if 10 equivalents of PEt$_3$ are added, a dramatic increase in catalytic activity is observed. The reaction profile shows a very fast initial phase followed by a period with no activity and a further period where the activity is restored but to a level lower than that of the initial phase. This behaviour is reproducible. Addition of water to the system leads to a similar reaction profile, although the overall rates are higher than in the absence of water. The catalyst present during the second phase of the reaction carried out in the presence of water does not appear to be deactivated and the conversion to carbonylation product at the end of the reaction shown in Fig. 2 is *ca.* 41%. Since the major product under these conditions is methyl ethanoate, this represents *ca.* 80% of the methanol being consumed.

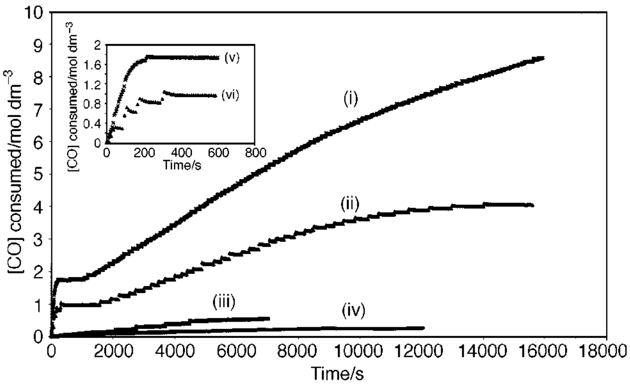

Fig. 1 CO uptake plots for methanol carbonylation reactions catalysed by: (i) [Cp*Co(CO)$_2$–PEt$_3$–H$_2$O; (ii) as (i) but no H$_2$O; (iii) as (ii), but no PEt$_3$; (iv) [Co$_2$(CO)$_8$]; inset: (v) and (vi) early stages of (i) and (ii), respectively.

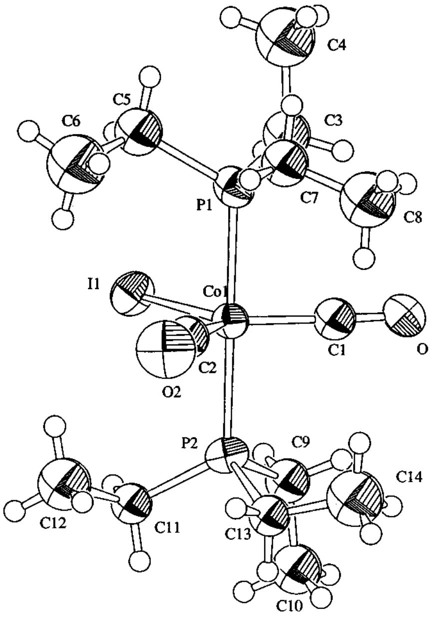

Fig. 2 X-Ray structure and numbering scheme for [CoI(CO)$_2$(PEt$_3$)$_2$]. Important bond lengths (Å) and angles (°): Co(1)–C(1) 1.75(2), Co(1)–C(2) 1.71(2), Co(1)–P(1) 2.208(6), Co(1)–P(2) 2.229(6), Co(1)–I(1) 2.649(3), C(1)–O(1) 1.14(2), C(2)–O(2) 1.17(2); I(1)–Co(1)–C(1) 114.4(7), I(1)–Co(1)–C(2) 118.6(7), I(1)–Co(1)–P(1) 89.5(2), I(1)–Co(1)–P(2) 89.9(2), C(1)–Co(1)–C(2) 127(1), C(1)–Co(1)–P(1) 89.7(7), C(1)–Co(1)–P(2) 89.8(7), C(2)–Co(1)–P(1) 90.5(7), C(2)–Co(1)–P(2) 90.5(7), P(1)–Co(1)–P(2) 179.0(3), Co(1)–C(1)–O(1) 175(1), Co(1)–C(2)–O(2) 173(2). There are two crystallographically distinct molecules in the asymmetric unit cell. The data for only one is reported here. The other is similar, except that only one ethyl group on one phosphine is *anti* to a Co–P bond.

Rates for the two phases of the reaction are presented in Table 1 and it should be noted that the conditions under which these reactions have been carried out are milder than those used for the industrial processes catalysed by rhodium or iridium systems. At 120 °C, the temperature of these studies, rates obtained with [RhCl(CO)$_2$]$_2$ as the catalyst precursor are of the order of 1 mol dm^{-3} h^{-1},[5] 44 times slower than the initial fast phase of the [Cp*Co(CO)$_2$]–PEt$_3$–H$_2$O system. The concentration of cobalt is 30 times that used for the rhodium catalyst so the actual activity of the cobalt system is 1.5 times the rate using rhodium. The high solubility and low cost of the cobalt system mean that it is possible to obtain industrially significant rates using the cobalt based system, even under the mild conditions used in this study.

GLC analysis of the liquid phase at the end of the reactions shows that the major product is methyl acetate, although acetic

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Table 1 Rates of carbonylation of methanol under various conditions[a]

Catalyst	[Catalyst]/ mol dm^{-3}	[PEt$_3$]/ mol dm^{-3}	[MeOH]/ mol dm^{-3}	[MeI]/ mol dm^{-3}	[H$_2$O]/ mol dm^{-3}	Solution volume/cm^3	Initial rate/ mol dm^{-3} h^{-1}	TOF[b]/h^{-1}
[$Co_2(CO)_8$]	0.15	0	20.5	2.8	0	44.1	0.64	4.3
[$Cp^*Co(CO)_2$]	0.09	0	24.5	0.15	0	51.6	0.32	3.6
[$Cp^*Co(CO)_2$]	0.15	1.5	22.3	1.9	0	87.8	18.3, 1.1[c]	123, 7.1[c]
[$Cp^*Co(CO)_2$]	0.15	1.5	22.2	1.8	4.5	4.3	43.9, 2.5[c]	314, 18[c]
[$CoI(CO)_2(PMe_2Ph)_2$][d]	2.7 × 10^{-3}	0	19.8	3.2	0	5.0	0.004	1.45
[$RhCl(CO)_2]_2$[e]	4.8 × 10^{-3}	0	—[f]	2.5	11.3	161	0.9[g]	188
[$RhCl(CO)_2]_2$[e]	4.8 × 10^{-3}	0	—[h]	2.4	2.3	164	0.6	125

[a] p_{CO} = 100 bar, T = 120 °C. Kinetic profiles were obtained using two different Hastelloy C autoclaves with different volumes. Reproducibility between the two reactors was checked by carrying out two identical reactions using identical concentrations. The reproducibility was ±15%. Reproducibility for the same autoclave was ±10%. [b] TOF is defined as the number of mol of CO consumed per mol of catalyst per hour. [c] Initial rate for the second active phase of the reaction. [d] Obtained from a 24 h batch reaction and analysis of the liquid phase products. [e] p_{CO} = 27 bar, but this reaction is zero order in p_{CO}. [f] Substrate added as methyl ethanoate (38.75 cm^3, 3.03 mol dm^{-3}), in ethanoic acid (64.9 cm^{-3}, 6.83 mol dm^{-3}); the reaction is zero order in [MeOH]. [g] Rises to 1.2 mol dm^{-3} as the reaction proceeds and [$RhI_2(CO)_2$]$^-$ forms.[6] [h] Substrate added as methyl ethanoate (23.82 cm^3, 1.83 mol dm^{-3}), in ethanoic acid (109.8 cm^{-3}, 11.4 mol dm^{-3}); the reaction is zero order in [MeOH].

acid is also formed, especially in the system containing added water. Traces of 1,1-dimethoxymethane (the acetal of ethanal) are also observed, but very much less than in the presence of [$Co_2(CO)_8$] based catalysts.

[$Cp^*Co(CO)_2$] reacts with *e.g.* PMe_3 to give [$Cp^*Co(CO)(PMe_3)$], which in turn reacts with iodomethane to give [$Cp^*Co(COMe)I(PMe_3)$].[7] Since there is no induction period for the initial phase of the reaction, this suggests that the initial fast step of the carbonylation reaction is catalysed by [$Cp^*Co(CO)(PEt_3)$]/[$Cp^*Co(COMe)I(PEt_3)$]. We have carried out IR studies on a final solution from a reaction carried out in the presence of water [ν_{CO} 1989, 1973 (sh), 1905 cm^{-1}] to try to identify the cobalt species present during the second, slower but more prolonged catalytically active phase, and in addition have isolated a complex from the final reaction solution in the absence of water.

The isolated complex has been characterised by X-ray crystallography‡ as [$CoI(CO)_2(PEt_3)_2$], a trigonal bipyramidal complex with axial PEt_3 ligands (Fig. 2). [$CoI(CO)_2(PEt_3)_2$] gives rise to the strong peak at 1905 cm^{-1}, together with a weaker peak at 1973 cm^{-1}. The origin of the absorption at 1989 cm^{-1} is unclear, but evidence from other reactions suggests that the species giving rise to it is catalytically active and may be [$Cp^*Co(CO)I$]$^-$. We have not isolated sufficient of [$CoI(CO)_2(PEt_3)_2$] to test its catalytic activity but the related [$CoI(CO)_2(PMe_2Ph)_2$] is active for methanol carbonylation (Table 1).

The isolation of [$CoI(CO)_2(PEt_3)_2$] from a solution containing excess MeI which would be expected efficiently to quaternise PEt_3 to [$PMeEt_3$]I, is surprising. However, we have shown by GCMS that free PEt_3 is present in the catalytic solutions and that the related [$CoI(CO)_2(PMe_2Ph)_2$] is formed if [$CpCo(PMe_2Ph)CO$] is used as a potential catalyst precursor, indicating either that phosphines can migrate between Co atoms without escaping the solvent cage, or that the solution can act as a source of free phosphine.

We conclude that careful design of cobalt based catalysts can give activities and selectivities that are comparable with those of their rhodium based analogues and because of the high solubility and low cost of the catalyst precursor, rates at low temperature can be higher than those currently observed under conditions used for the commercial rhodium or iridium based processes.

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Notes and references

‡ *Crystal data*: [$C_{14}H_{30}O_2CoIP_2$], M_r = 478.18, orthorhombic, space group $P2_12_12_1$, a = 15.95(1), b = 19.482(9), c = 13.312(10) Å, U = 4136(4) Å^3, Z = 8, D_c = 1.563 g cm^{-3}, F(000) = 1920.00, μ(Mo-Kα) = 24.58 cm^{-1}, λ = 0.71069 Å, T = 230 K. Crystal size, 0.3 × 0.25 × 0.2 mm. Of the 1917 reflections that were collected, $3 < 2\theta < 40.0°$ on a Rigaku AFC7S diffractometer, 1622 were observed. Structure solved by direct methods and expanded using Fourier techniques. The Co, I, P and O atoms were refined anisotropically, the C atoms isotropically. The maximum and minimum residual electron densities are 0.62 and −0.42 e A^{-3}. R = 0.040, R_w = 0.037. CCDC 182/1282.

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