Cis-[$RhI(CO)(Ph_2PCH_2P(S)Ph_2)$]: A New Catalyst for Methanol Carbonylation

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The complex *cis*-[$RhI(CO)(Ph_2PCH_2P(S)Ph_2)$] is eight times more active than the classic Monsanto catalyst [$RhI_2(CO)_2$]$^-$ for the carbonylation of methanol at 185 °C offering the first promoted system effective under conditions which allow industrially realistic rates; the X-ray crystal structure of the analogue *cis*-[$RhCl(CO)(Ph_2PCH_2P(S)Ph_2)$] is reported together with *in situ* spectroscopic evidence for species in the catalytic cycle.

More than twenty-five years after its discovery, the Monsanto catalyst [$RhI_2(CO)_2$]$^-$ is still the preferred commercial catalyst for the carbonylation of methanol to acetic acid.[1] Attempts to modify this catalyst and increase its activity by introducing electron-donating ligands have been hampered by the instability of many complexes of such ligands under the harsh reaction conditions required for carbonylation. Recent reports[2–4] have identified a number of mixed-donor ligands which promote carbonylation under very mild reaction conditions (typically < 130 °C and < 20 bar). However, these mild conditions are not well suited to commercial operation where high absolute reaction rates are required and engineering constraints favour higher temperatures and therefore higher pressures.

We have found that the use of the diphosphinesulfide $Ph_2PCH_2P(S)Ph_2$ as a promoter for rhodium catalysed methanol carbonylation allows a surprisingly substantial rate increase under industrially feasible conditions. Comparison of the carbonylation rate in an experiment using $Ph_2PCH_2P(S)Ph_2$ (Table 1, run 1) with reactions employing either no ligand (run 2) or using PPh_3 and/or $P(S)Ph_3$ (runs 3–5) shows the efficacy of $Ph_2PCH_2P(S)Ph_2$ as a promoter. The closely related ligands $Ph_2PCH_2CH_2P(O)Ph_2$,[2,3] $Ph_2PCH_2P(O)Ph_2$[3] and $Ph_2PN(Ph)P(S)Ph_2$[4] give only small improvements over [$RhI_2(CO)_2$]$^-$ under these conditions (runs 6–8).

Our initial experiments were carried out using a ligand : rhodium ratio of 4 : 1 but we observed the optimum rate enhancement when the discrete complex *cis*-[$RhCl(CO)(Ph_2PCH_2P(S)Ph_2)$] **1** was used as pre-catalyst (run 9). We believe that any phosphine present in excess of this 1 : 1 ligand : rhodium ratio quaternises with MeI and that ionic iodide inhibits rate; addition of 3 equiv. of [$P(Me)Ph_3$]I to an experiment using **1** as pre-catalyst causes a similar retardation in rate. Complex **1** is readily formed on mixing [$RhCl(CO)_2$]$_2$ with 2 equiv. of $Ph_2PCH_2P(S)Ph_2$ in MeOH; we have seen no evidence for the formation of dimeric complexes[5] in this reaction. We have unambiguously characterised **1** by NMR and IR spectroscopy† and by single crystal X-ray analysis‡ (Fig. 1) of its dichloromethane solvate. The structure confirms the stereochemistry at rhodium in which the phosphorus lies *trans* to the chloride and sulfur lies *trans* to the carbonyl ligand, but shows no unusual features to explain the unexpected stability of the catalyst at high temperatures.

Table 1 Carbonylation experiments[a]

Run	Ligand	Ligand : Rh ratio	Rate[b]/ mol l^{-1} h^{-1}
1	$Ph_2PCH_2P(S)Ph_2$	4	14.2
2	—	—	2.3
3	PPh_3	4	2.6
4	$P(S)Ph_3$[c]	4	3.5
5	PPh_3 + $P(S)Ph_3$[c]	4 + 4	3.8
6	$Ph_2PCH_2CH_2P(O)Ph_2$	4	2.7
7	$Ph_2PCH_2P(O)Ph_2$	4	3.0
8	$Ph_2PN(Ph)P(S)Ph_2$	4	3.5
9	$Ph_2PCH_2P(S)Ph_2$	1[d]	19.6

[a] Conditions used: A solution of MeOH (0.708 mol), MeC(O)OH (0.996 mol) and MeI (0.048 mol) was heated to 185 °C under CO in a stirred 150 cm^3 Hastelloy™ B2 autoclave. A slurry of ligand mixed with [$RhCl(CO)_2$]$_2$ (0.237 mmol) in MeOH (0.156 mol) was then injected and simultaneously the autoclave was pressurised to 70 bar with CO. The rate of carbonylation was monitored by recording the rate of CO uptake from a reservoir. In each case the only liquid product detected by gas chromatography was MeC(O)OH. [b] The rates given are average rates to the point at which half the MeOH has been consumed. [c] $P(S)Ph_3$ was included in the initial autoclave charge and was not present in the slurry injected into the autoclave. [d] Mixing 2 equiv. of $Ph_2PCH_2P(S)Ph_2$ with 1 equiv. of [$RhCl(CO)_2$]$_2$ in MeOH gives exclusively *cis*-[$RhCl(CO)(Ph_2PCH_2P(S)Ph_2)$].

During carbonylation under the conditions of Table 1 the only rhodium carbonyl species observed by IR spectroscopy is *cis*-[$RhI(CO)(Ph_2PCH_2P(S)Ph_2)$] **2**, the iodo analogue of **1**. The position of the carbonyl stretch in the IR spectrum† suggests

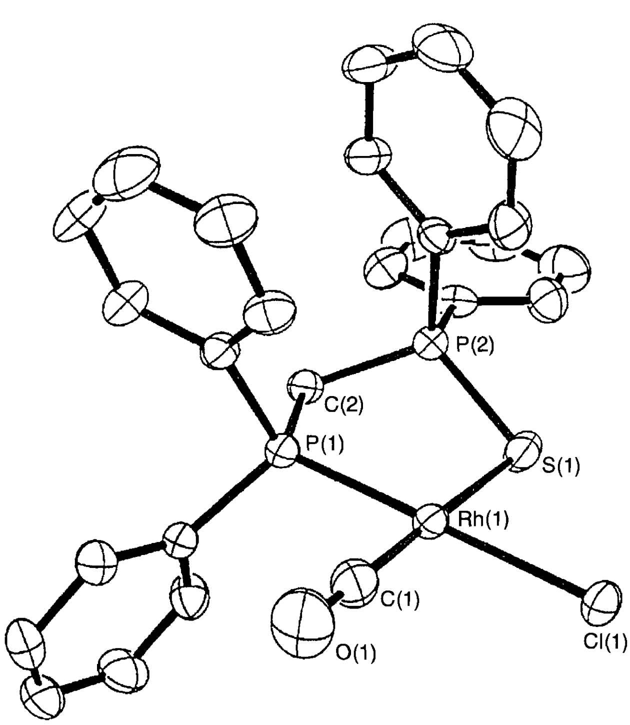


Fig. 1 Molecular structure of **1** showing atom labelling scheme. Non-hydrogen atoms are represented as ellipsoids enclosing 30% probability density. All hydrogens have been omitted for clarity. Important dimensions include; bond lengths (Å): Rh(1)–P(1) 2.220(2), Rh(1)–S(1) 2.403(2), Rh(1)–Cl(1) 2.401(2), Rh(1)–C(1) 1.826(8), P(2)–S(1) 2.005(3), P(2)–C(2) 1.808(7), P(1)–C(2) 1.866(6), O(1)–C(1) 1.144(11); bond angles (°): P(1)–Rh(1)–S(1) 92.7(1), P(1)–Rh(1)–Cl(1) 179.4(1), S(1)–Rh(1)–Cl(1) 86.7(1), P(1)–Rh(1)–C(1) 87.8(3), S(1)–Rh(1)–C(1) 179.0(3), Cl(1)–Rh(1)–C(1) 92.7(3), Rh(1)–S(1)–P(2) 98.6(1), S(1)–P(2)–C(2) 108.0(2), P(1)–C(2)–P(2) 106.1(3), Rh(1)–P(1)–C(2) 111.3(2), Rh(1)–C(1)–O(1) 177.7(8); torsion angles (°): Rh(1)–P(1)–C(2)–P(2) −31.3(3), P(1)–C(2)–P(2)–S(1) 50.9(3), C(2)–P(2)–S(1)–Rh(1) −45.6(2), P(2)–S(1)–Rh(1)–P(1) 22.7(1), C(2)–P(1)–Rh(1)–S(1) 2.8(2).

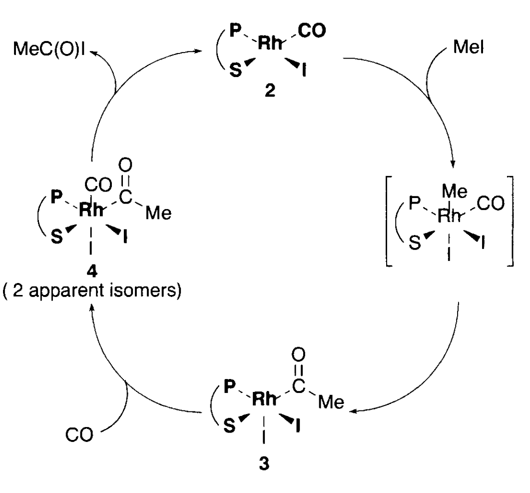
that **2** is more electron-rich than $[\mathrm{RhI_2(CO)_2}]^-$; this feature may contribute to the higher carbonylation rate observed with **2**. The carbonylation rate is first order in [MeI], consistent with **2** being the resting state in the catalytic cycle, and is independent of CO pressure above a threshold of 50 bar.

For runs 1 and 9, Table 1, a high reaction rate is sustained up to the point where half of the substrate has been consumed, after which the rate falls. In separate experiments, addition of a second aliquot of MeOH to a completed carbonylation experiment allows a resumption of the enhanced rate, indicating that catalyst lifetime is longer than the duration of one carbonylation experiment.

In model NMR studies in $\mathrm{CD_2Cl_2}$ at room temperature† (Scheme 1), complex **2** reacts with MeI to give $[\mathrm{Rh(C(O)CH_3)I_2(Ph_2PCH_2P(S)Ph_2)}]$ **3**. Even though it is possible to follow the progress of this reaction by NMR (by periodically arresting the reaction by cooling to −60 °C in order to record spectra), we were not able to detect the $\mathrm{Rh^{III}}$-methyl intermediate.

When placed under CO (30 bar), a $\mathrm{CD_2Cl_2}$ solution of complex **3** gives two apparent isomers of $[\mathrm{Rh(C(O)CH_3)I_2(CO)(Ph_2PCH_2P(S)Ph_2)}]$ **4a** and **4b** in an approximate ratio of 2 : 1. Reaction of **2** with MeI under CO (40 bar) gives **4a** and **4b** directly in the same ratio. The use of $^{13}\mathrm{CO}$ and $^{13}\mathrm{CH_3I}$ in the formation of **3** and **4** allowed the observation of their characteristic rhodium–acetyl[6,7] and rhodium–carbonyl[7] $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR resonances. In **3**, **4a** and **4b** the magnitude of $^1J(\mathrm{RhP})$ (values between 126 and 135 Hz) suggests an iodide ligand *trans* to phosphorus; the absence of any large value of $^2J(\mathrm{CP})$ (values are between 2 and 4 Hz) suggests further that the acetyl group in **3**, and both acetyl and CO groups in **4**, are *cis* to phosphorus. Beyond this, it is not possible either definitively to assign the stereochemistry of **3**, or to identify the structures of **4a** or **4b**. For **4** there are six possible isomeric structures consistent with the characterising data representing three pairs of enantiomers, and we suggest that **4a** and **4b** are two of these pairs.

Reductive elimination of acetyl iodide from **4** completes the catalytic cycle and is observed by NMR. Moreover, addition of acetyl chloride to **2** gives $[\mathrm{Rh(C(O)CH_3)ClI(CO)(Ph_2PCH_2P(S)Ph_2)}]$; this complex can also be generated from **1**, MeI and CO, with eventual liberation of acetyl chloride. In separate experiments we have obtained IR spectroscopic data consistent with the structures proposed for **2**, **3** and **4**.† In these model studies we have seen no evidence for hemilabile behaviour, which has been suggested to be important for catalysis employing mixed-donor ligands.[2,8]



Scheme 1 P⌒S = $\mathrm{Ph_2PCH_2P(S)Ph_2}$. The relative dispositions of ligands in bold type are defined by the NMR data.

Although we have not yet assessed the long-term stability of this catalyst system, these results show for the first time that a discrete rhodium–phosphine complex can give a significant improvement in carbonylation activity over $[\mathrm{RhI_2(CO)_2}]^-$ under conditions which allow industrially realistic rates.

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Footnotes

† *Selected spectroscopic data*: (All NMR spectra were recorded in $\mathrm{CD_2Cl_2}$. **3′**, **4a′** and **4b′** are the ^{13}C-labelled analogues of **3**, **4a** and **4b**; *i.e.* **3′** contains a $^{13}\mathrm{CO}^{13}\mathrm{CH_3}$ group, **4a′** and **4b′** contain ^{13}CO and $^{13}\mathrm{CO}^{13}\mathrm{CH_3}$ groups.) For **1**: $^{31}\mathrm{P}\{^1\mathrm{H}\}$: δ(P) 48.3 (dd), δ (P=S) 52.2 (dd), $^1J(\mathrm{RhP})$ 159 Hz, $^2J(\mathrm{RhP})$ 1 Hz, $J(\mathrm{PP})$ 49 Hz; $\nu(\mathrm{CO})/\mathrm{cm^{-1}}$ $(\mathrm{CH_2Cl_2})$ 1992. For **2**: $^{31}\mathrm{P}\{^1\mathrm{H}\}$: δ(P) 50.6 (dd), δ(P=S) 61.3 (dd), $^1J(\mathrm{RhP})$ 164 Hz, $^2J(\mathrm{RhP})$ 2 Hz, $J(\mathrm{PP})$ 60 Hz; $\nu(\mathrm{CO})/\mathrm{cm^{-1}}$ $(\mathrm{CH_2Cl_2})$ 1988. For **3′**: $^{31}\mathrm{P}\{^1\mathrm{H}\}$: δ(P) 55.4 (ddd), δ(P=S) 58.2 (dd), $^1J(\mathrm{RhP})$ 135 Hz, $^2J(\mathrm{RhP})$ 4 Hz, $J(\mathrm{PP})$ 47 Hz, $^2J(\mathrm{CP})$ 4 Hz; $^{13}\mathrm{C}\{^1\mathrm{H}\}$: δ(*C*OCH$_3$) 212.5 (ddd), δ(CO*C*H$_3$) 48.9 (d), $^1J(\mathrm{RhC})$ 25 Hz, $^1J(\mathrm{CC})$ 33 Hz; ^{1}H: δ(COCH$_3$) 3.18 (dd), $^1J(\mathrm{CH})$ 133 Hz, $^2J(\mathrm{CH})$ 6 Hz; $\nu(\mathrm{CO})/\mathrm{cm^{-1}}$ $(\mathrm{CH_2Cl_2})$ 1697. For **4a′**: $^{31}\mathrm{P}\{^1\mathrm{H}\}$: δ(P) 27.6 (ddm), δ(P=S) 50.3 (d), $^1J(\mathrm{RhP})$ 129 Hz, $J(\mathrm{PP})$ 27 Hz, $^2J(\mathrm{CP})$ 2 Hz; $^{13}\mathrm{C}\{^1\mathrm{H}\}$: δ (*C*OCH$_3$) 219.4 (dd), δ(CO) 177.8 (d), δ(CO*C*H$_3$) 51.8 (d), ^1J[RhC(acetyl)] 22 Hz, $^1J(\mathrm{CC})$ 31 Hz, ^1J[RhC(carbonyl)] 68 Hz; ^{1}H: δ(COCH$_3$) 3.04 (dd), $^1J(\mathrm{CH})$ 132 Hz, $^2J(\mathrm{CH})$ 6 Hz. For **4b′**: $^{31}\mathrm{P}\{^1\mathrm{H}\}$: δ(P) 35.5 (ddm), δ(P=S) 59.9 (dm) $^1J(\mathrm{RhP})$ 126 Hz, $^2J(\mathrm{RhP})$ 3 Hz, $J(\mathrm{PP})$ 42 Hz, $^2J(\mathrm{CP})$ 3 Hz, $^3J(\mathrm{CP{=}S})$ 3 Hz; $^{13}\mathrm{C}\{^1\mathrm{H}\}$: δ(*C*OCH$_3$) 219.8 (dd), δ(CO) 181.8 (d), δ(CO*C*H$_3$) 46.0 (d), ^1J[RhC(acetyl)] 22 Hz, $^1J(\mathrm{CC})$ 30 Hz, ^1J[RhC(carbonyl)] 68 Hz; ^{1}H: δ(COCH$_3$) 2.93 (dd), $^1J(\mathrm{CH})$ 131 Hz, $^2J(\mathrm{CH})$ 6 Hz. For **4**: $\nu(\mathrm{CO})/\mathrm{cm^{-1}}$ $(\mathrm{CH_2Cl_2})$ 2081, 1685 (**4a** and **4b** are indistinguishable by IR spectroscopy).

‡ *Crystal data* for **1**·$\mathrm{CH_2Cl_2}$: $\mathrm{C_{27}H_{24}Cl_3OP_2RhS}$, M_r = 667.7, monoclinic, space group $P2_1/c$ (No. 14), a = 8.929(2), b = 16.647(4), c = 20.083(4) Å, β = 102.11(2)°, U = 2919(1) Å^3, Z = 4, D_x = 1.52 g cm^{-3}, $\bar{\lambda}$ = 0.71073 Å, μ(Mo-Kα) = 1.06 mm^{-1}, $F(000)$ = 1344, T = 295 K. Data were collected on a Siemens R3m diffractometer for a unique quadrant of reciprocal space with $4 < 2\theta < 50°$. The structure was solved by heavy atom methods and refined by least-squares analysis to R 0.051 for 3514 unique, observed [$I > 2\sigma(I)$], absorption corrected, intensity data. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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