

Novel Catalysts for the Carbonylation of Methanol

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Rhodium(I) carbonyl complexes containing phosphino-thiolate and -thioether ligands are almost four times as active in catalysing the carbonylation of methanol to ethanoic acid as the previously known catalyst, $[\text{RhI}_2(\text{CO})_2]^-$; the crystal structure of one procatalyst, $[\text{Rh}(\text{SC}_6\text{H}_4\text{PPh}_2)(\text{CO})]_2$, is reported.

The rhodium-catalysed carbonylation of methanol is a process of great industrial importance, with 60% of the estimated 5.6 million tonnes *per annum* global ethanoic acid production capacity being based on this technology.¹ The process is also of considerable theoretical interest, as the catalytic cycle is simple and well understood, with all the proposed intermediates having been detected.² However, in the 25 years since the first reports of catalysis,³ there has been little improvement on the intrinsic activity of the rhodium catalyst, $[\text{RhI}_2(\text{CO})_2]^-$. Attempts to develop new catalyst species have been hampered by the relatively harsh conditions under which the reaction is conducted commercially (150–200 °C, 25–45 atm, in the presence of I^-): under these conditions, virtually any source of rhodium will be converted to $[\text{RhI}_2(\text{CO})_2]^-$.⁴ However, a novel methanol carbonylation catalyst containing a diphosphine monosulfide ligand was recently described^{5,6} which showed a large improvement in absolute rate over that obtainable with $[\text{RhI}_2(\text{CO})_2]^-$, in contrast to catalysts developed for use under milder conditions.⁷ We describe here two further new classes of improved methanol carbonylation catalysts which show significant improvements in absolute rates over those obtained with $[\text{RhI}_2(\text{CO})_2]^-$.

The complexes **1** and **2** are formed as air-stable solids by the reaction of the appropriate ligand with $[\text{RhCl}(\text{CO})_2]_2$ in the presence of base.[†] Use of a large excess of ligand leads to brown rhodium(III) complexes which we have described previously.⁸ The compounds are moderately soluble in acetone and toluene, but only sparingly soluble in alcohols and insoluble in ethereal solvents and alkanes. The compounds show only a single $\nu(\text{C}\equiv\text{O})$ band and only a single ³¹P NMR signal: these and other data are consistent with the dimeric structure shown, which has been confirmed by X-ray crystallographic studies[‡] in the case of **1**.

The crystal structure of **1** (as crystallised from $[\text{D}_6]_6\text{acetone}$) is shown in Fig. 1. The rhodium atoms are approximately square-planar, coordinated by phosphorus, carbonyl carbon and two bridging sulfur atoms. The chelated S–Rh distance, 2.360(2) Å, is only slightly shorter than the non-chelated distance, 2.386(2) Å. The rhodium atom lies 0.595(1) Å out of the P–phenylene–S plane, a typical distance for this type of complex.⁸

The Rh_2S_2 ring (or bridge system) is bent, with a dihedral angle of 109.30(9)° between the least squares planes around rhodium and of 115.13(7)° across the Rh–Rh vector. The Rh–Rh distance, 2.980(1) Å, is typical of thiolate-bridged Rh^I complexes,¹¹ and might suggest a weak bonding interaction. The Rh–S–Rh' angle of 77.77(7)° is small but not atypical.¹¹

In the crystal lattice the rhodium and sulfur atoms are in very exposed positions but do not form any short intermolecular contacts: the shortest contacts are to phenyl hydrogen atoms in a neighbouring molecule, *i.e.* Rh...H(34*) 3.243(1) Å, S...H(34*) 3.482(2) Å, S...H(33*) 3.039(2) Å. This may be indicative of considerable electron density on the *exo* face of the molecule, and consequently a high Lewis basicity, particularly on the bridging sulfur atoms. It is also notable that the P–phenylene–S plane is inclined towards the *endo* face of the Rh_2S_2 butterfly, increasing the exposure of the rhodium atom still further.

The results of batch carbonylations of methanol are shown in Fig. 2: curve (a) shows the course of the reaction catalysed by $[\text{RhI}_2(\text{CO})_2]^-$, which is formed *in situ* from the added $[\text{RhCl}(\text{CO})_2]_2$ under the reaction conditions.⁴ The reaction curves in Fig. 2 show substantial deviations from linearity even in the early portions: numerical differentiation by the methods of Southern¹² yields the turnover numbers shown in Table 1. It can be seen that the maximum rate of the reaction catalysed by **2** is four times that of the $[\text{RhI}_2(\text{CO})_2]^-$ catalysed reaction. The phosphinothioether complexes **3** and **4** are also catalysts for the carbonylation of methanol, with comparable activity to the corresponding thiolate complexes. The solutions remaining at the end of the reactions were analysed by GLC: the only liquid product detected was ethanoic acid.

Oxidative addition of iodomethane to **4b** yields the rhodium(III) acyl complex **6**,[¶] presumably through the intermediacy of the methylrhodium(III) complex **5**. The facile migratory insertion of carbon monoxide during oxidative addition of iodomethane to carbonylrhodium(I) centres is well known.¹⁷ A chloro-analogue of **7** can be formed by the prolonged reaction of **4b** with ethanoyl chloride: only one of the

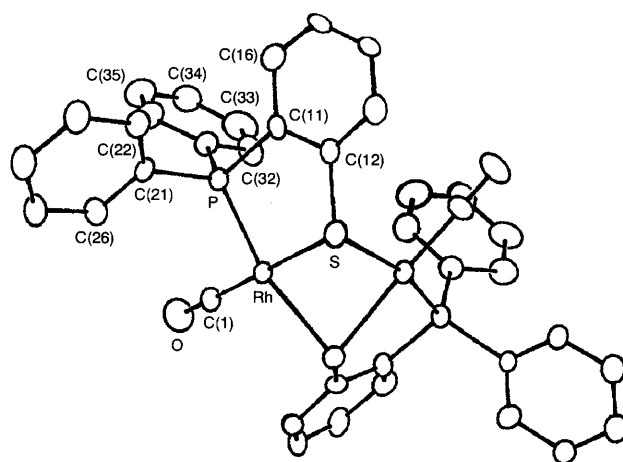
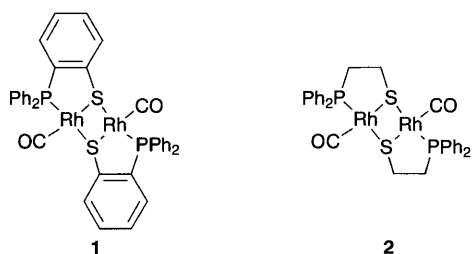


Fig. 1 The molecular structure of **1**·2(CD₃)₂CO, as determined by single crystal X-ray diffraction, showing atomic labelling. The molecule lies on a crystallographic twofold axis, and unlabelled atoms are related to labelled atoms. All hydrogen atoms have been omitted for clarity, as has the associated solvent molecule. Important dimensions include: interatomic distances (Å) Rh–P 2.217(2), Rh–C 1.84(1); interatomic angles (°) S–Rh–S' 82.14(9), S–Rh–P 85.65(8), S'–Rh–P 165.37(8), S–Rh–C(1) 100.0(3), P–Rh–C(1) 92.6(3).

five possible isomers appears to be formed,¹¹ although we are currently uncertain of the absolute stereochemistry.

On the basis of these observations, we propose the mechanism shown in Fig. 3 to explain the catalysis by **4**. This is similar to the cycle proposed for catalysis by $[\text{Rh}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{PSPPh}_2)]$, in which intermediates analogous to **6** and **7** have been detected spectroscopically.⁶ Both mechanisms are very similar to the cycle for catalysis by $[\text{RhI}_2(\text{CO})_2]^-$,²

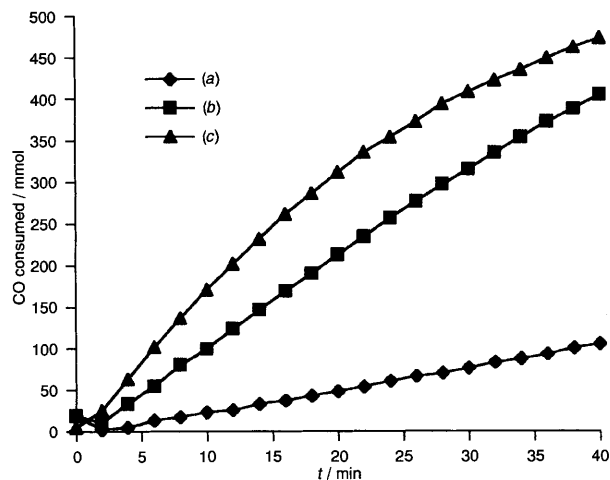


Fig. 2 Carbonylation of methanol with (a) $[\text{RhI}_2(\text{CO})_2]^-$ (formed from added $[\text{RhCl}(\text{CO})_2]_2$); (b) **1**; (c) **2**. MeOH (27.7 g), AcOH (59.8 g), MeI (6.8 g), catalyst (474 μmol Rh); $P = 70$ bar; $T = 185$ °C

Table 1 Maximum turnover numbers observed during methanol carbonylation (conditions as for Fig. 2)

Catalyst	Max. turnover/h ⁻¹
$[\text{RhI}_2(\text{CO})_2]^-$	450
1	1300
2	1800
3a	1000
4a	1500

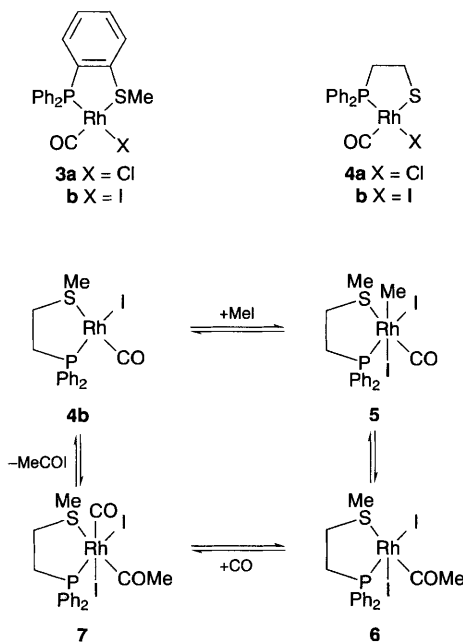


Fig. 3 Proposed mechanism of catalysis of methanol carbonylation by **4**. The mechanism of catalysis by **3** is thought to be analogous. The stereochemistries of the intermediates have not been determined.

except that all the species are neutral rather than anionic. This is surprising, as it is the anionic charge on $[\text{RhI}_2(\text{CO})_2]^-$ which has been advanced as an explanation of its high reactivity towards iodomethane.¹⁸ Our results indicate however, that high reaction rates towards iodomethane can be achieved in a neutral rhodium(I) complex with appropriate phosphorus and sulfur donors: that negative charge does not equate with nucleophilicity, especially in 'soft' systems, has already been discussed by other authors.¹⁹

The reaction of iodomethane with **1** and **2** is much more complex and solvent dependent. The main product from **1** on prolonged standing in ethanoic acid with 4 equiv. of iodomethane at room temp. and under 1 bar CO is **3b**.^{**} Transition metal phosphinothiolate complexes are known to undergo facile *S*-methylation on treatment with iodomethane to give phosphinothioether complexes.²⁰ However, since binuclear species are also formed from the reaction of **1** and **2** with iodomethane under other conditions, the exact catalytic mechanism in these systems is currently unclear, although it seems likely that a cycle analogous to that in Fig. 3 is involved. Whatever the exact nature of the catalytic intermediates, the ³¹P NMR spectrum of the inorganic residue remaining after the end of a batch carbonylation of methanol catalysed by **2** indicates that a high proportion of the phosphorus remains bound to the rhodium centre even after heating at 185 °C for 3 h in the presence of a large excess of iodomethane.

J. R. D. and N. W. are indebted to BP Chemicals Ltd for generous financial support, including a studentship for N. W., and for the gift of $[\text{RhCl}(\text{CO})_2]_2$ and $[\text{RhI}(\text{CO})_2]_2$. The authors also thank Mr C. Lu for his help in collecting X-ray diffraction data and the European Social Fund for financial support to N. W. during the initial period of this work.

Received, 31st January 1995; Com. 5/00559K

Footnotes

† Dicarboxylbis[μ -2-(diphenylphosphino)benzenethiolato-*P*, μ -*S*]dirhodium(I) **1**: $[\text{RhCl}(\text{CO})_2]_2$ (150 mg, 385 μmol) was added to a solution of 2-(diphenylphosphino)benzenethiol⁹ (220 mg, 747 μmol) and lithium methoxide (70 mg, 1.8 mmol) in methanol (25 ml). The mixture was stirred for 30 min and a red-orange precipitate isolated (287 mg, 88%). Satisfactory elemental analysis were obtained for **1**, **2**, **3a**, **4a** and **6**. $\nu_{\text{max}}/\text{cm}^{-1}$ 1946 (CO). δ_{P} [109.3 MHz, solvent $(\text{CD}_3)_2\text{CO}$, standard 85% H_3PO_4 (ext.)] +60.5 [d, J_{PRh} 158 Hz].

Dicarboxylbis[μ -2-(diphenylphosphino)ethanethiolato-*P*, μ -*S*]dirhodium(I) **2**: $[\text{RhCl}(\text{CO})_2]_2$ (150 mg, 385 μmol) was added to a solution of lithium 2-(diphenylphosphino)ethanethiolate¹⁰ (747 μmol) in diethyl ether (25 ml). The mixture was stirred for 30 min and an orange precipitate isolated (264 mg, 91%). M 752. $\nu_{\text{max}}/\text{cm}^{-1}$ 1947 (CO). δ_{P} [109.3 MHz, solvent $(\text{CD}_3)_2\text{CO}$, standard 85% H_3PO_4 (ext.)] +63.7 [d, J_{PRh} 158 Hz].

‡ Crystal data for **1**- $2(\text{CD}_3)_2\text{CO}$: $\text{C}_{38}\text{H}_{28}\text{O}_2\text{P}_2\text{Rh}_2\text{S}_2 \cdot 2\text{C}_3\text{D}_6\text{O}$, $M_r = 976.64$, monoclinic, space group $C2/c$, $a = 26.14(3)$, $b = 8.887(7)$, $c = 21.94(3)$ Å, $\beta = 121.57(5)^\circ$, $U = 4344(8)$ Å³, $Z = 4$, $D_c = 1.49$ g cm⁻³, $F(000) = 1952$, $\mu(\text{Mo-K}\alpha) = 0.951$ mm⁻¹, $T = 291$ K. A crystal of **1** was grown from a solution in $[\text{D}_6]_2$ acetone. A total of 7951 reflections were collected ($3^\circ \leq 2\theta \leq 50^\circ$) on an Enraf-Nonius CAD4 diffractometer: the structure was solved using heavy-atom methods (MOLLEN), locating all the non-hydrogen atoms. All non-hydrogen atoms in the complex were refined anisotropically, with the solvate non-hydrogen atoms being refined isotropically. Hydrogen atoms were placed in calculated positions, and not refined. The final R for 2618 reflections with $F > 3.0\sigma(F_o)$ was 0.064. 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.

§ Carbonylchloro[diphenyl(2-methylthiophenyl)phosphine]rhodium(I) **3a**: Diphenyl(2-methylthiophenyl)phosphine¹³ (238 mg, 772 μmol) was dissolved in methanol (25 ml), and a solution of $[\text{RhCl}(\text{CO})_2]_2$ (150 mg, 386 μmol) in a minimum quantity of methanol was added. The mixture was stirred for 30 min, and a brown precipitate isolated (179 mg, 49%). $\nu_{\text{max}}/\text{cm}^{-1}$ 1998 (CO). δ_{P} [109.3 MHz, solvent CDCl_3 , standard 85% H_3PO_4 (ext.)] +70.3 [d, J_{PRh} 158 Hz].

Carbonylchloro[diphenyl(2-methylthioethyl)phosphine]rhodium(I) **4a**:¹⁴ Diphenyl(2-methylthioethyl)phosphine¹⁵ (201 mg, 772 μmol) was dis-

solved in methanol (25 ml). A solution of $[\text{RhCl}(\text{CO})_2]_2$ (150 mg, 386 μmol) in minimum quantity of methanol was added, and the mixture stirred for 30 min. A brown precipitate was isolated (191 g, 58%). $\nu_{\text{max}}/\text{cm}^{-1}$ 1984 (CO). δ_{P} [109.3 MHz, solvent CDCl_3 , standard 85% H_3PO_4 (ext.)] +72.7 [d, J_{PRh} 162 Hz].

¶ Carbonyl[diphenyl(2-methylthioethyl)phosphine]iodorhodium(I) **4b**: prepared as the chloro analogue above using $[\text{RhI}(\text{CO})_2]_2$ (221 mg, 386 μmol), yielding a brown solid (225 mg, 55%). $\nu_{\text{max}}/\text{cm}^{-1}$ 1982 (CO). δ_{P} [109.3 MHz, solvent CDCl_3 , standard 85% H_3PO_4 (ext.)] +72.7 [d, J_{PRh} 162 Hz].

[Diphenyl(2-methylthioethyl)phosphine]ethanoyldiiodorhodium(III) **6**: **4b** (100 mg, 187 μmol) was dissolved in iodomethane (1 ml) and the mixture stirred for 30 min. Diethyl ether (5 ml) was added, and the mixture stirred for a further 5 min. A light-brown precipitate was isolated (112 mg, 88%). $\nu_{\text{max}}/\text{cm}^{-1}$ 1642 (CO). δ_{P} [109.3 MHz, solvent CDCl_3 , standard 85% H_3PO_4 (ext.)] +49.2 [d, J_{PRh} 101 Hz]. Reaction of ^{13}C iodomethane with a solution of **4b** in CDCl_3 yielded a solution of **6** which was identified by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. δ_{C} [67.9 MHz, solvent CDCl_3 , standard SiMe_4] 68.0 (s, COCH_3).

|| Two isomers of the analogous compounds are observed^{2,6} in the catalytic cycles of $[\text{RhI}_2(\text{CO})_2]^-$ and $[\text{RhI}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{PSPPh}_2)]$.

** **1** (13 mg, 16 μmol) was dissolved in ethanoic acid (0.8 ml) and $^{2}\text{H}_6$ -acetone (0.2 ml) under an atmosphere of carbon monoxide. ^{13}C -Iodomethane (4 μl , 64 μmol) was added, and the mixture allowed to stand at room temperature for 3 days. Complex **3b** was identified by comparison with a sample prepared from $[\text{RhI}(\text{CO})_2]_2$ and diphenyl(2-methylthioethyl)phosphine. δ_{P} [109.3 MHz, solvent CDCl_3 , standard 85% H_3PO_4 (ext.)] +68.4 [dd, J_{PRh} 121 Hz, J_{PC} 6.0 Hz].

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