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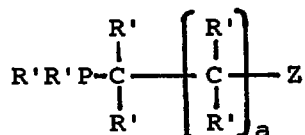


**PROCESS FOR THE CARBONYLATION OF METHANOL OR A REACTIVE DERIVATIVE
THEREOF**

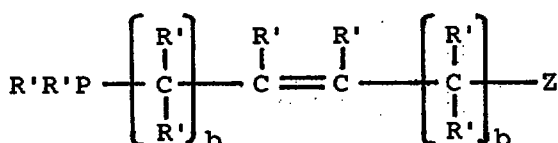
The present invention relates to a process for the carbonylation of methanol or a reactive derivative thereof in the presence of a halide promoter and a catalyst system comprising a rhodium component and a bidentate phosphorus-sulphur ligand. The present invention also relates to novel rhodium complexes.

The preparation of rhodium (I) and rhodium (II) complexes with mixed sulphur-nitrogen, -phosphorus and -arsenic ligands is described by H A Hodali and I.M. Kittaneh in Dirasat:Nat.Sci. (Univ. Jordan), 1983 10 47-55; CA., 1983 101 16218s.

US Patent 4,670,570 describes a process for the production of carboxylic acids from alcohols in the presence of a catalyst system consisting essentially of rhodium metal atom, a phosphorus containing ligand and a halogen-containing compound as promoter. According to US 4,670,570 in the phosphorus containing ligand at least one oxo (=O) oxygen atom is attached to a phosphorus atom or a carbon atom to form a Z group and the P=O or C=O group in said Z group is located at least one carbon atom removed and preferably from 2-4 carbon atoms removed from the phosphorus atom of the molecules represented by the formulas :



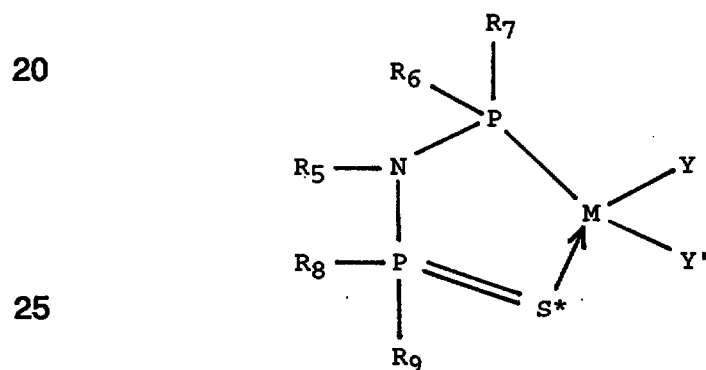
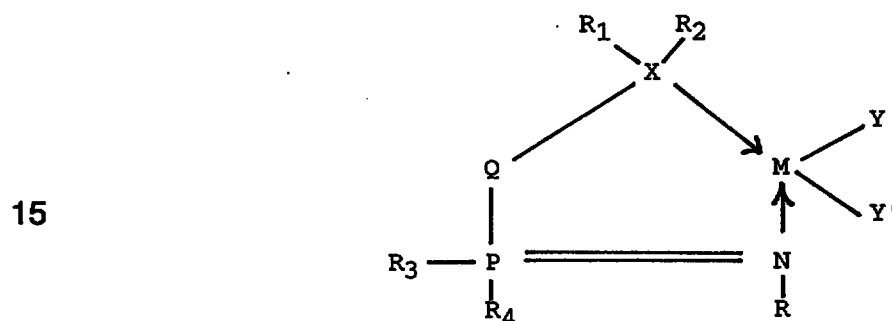
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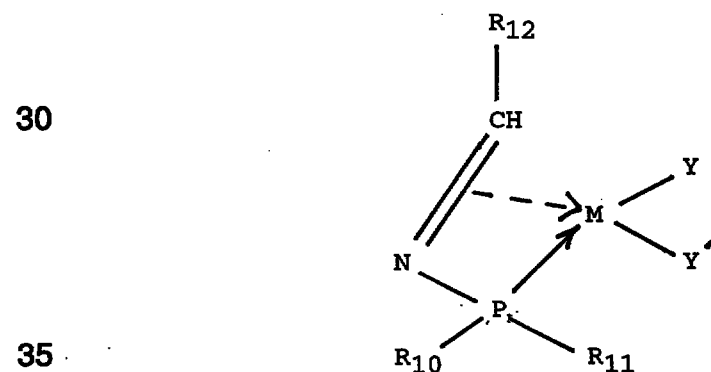


An especially preferred ligand is said to be
 $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(=\text{O})\text{Ph}_2$.

International application publication number WO 92/04118
 describes novel catalyst precursors having a phosphorus-nitrogen
 5 chelated ligand attached to a metal, where said metal is most
 preferably Rh, Ni or Co. The chelated ligand comprises a
 substantially unreactive connecting backbone structure which links
 two different dative centres or a donor with an anionic site.
 According to WO 92/04118 the catalyst precursor has the general
 10 formula:



or





wherein M is a Group VIII B transition metal

Y, Y' are the same or different selected from CO, Cl⁻, phosphines and olefinic hydrocarbons,

5 R₁₋₄, R₆₋₁₂ are the same or different non-reactive substituents,

Q is selected from (CH₂)_n where n=1-5, a benzene ring connected to P and X in the o-positions, an olefin connected to P and X across the double bond, and (CH₃)CH

X is P or As

10 R = a substituted aromatic ring, A B



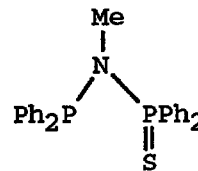
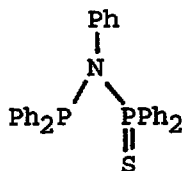
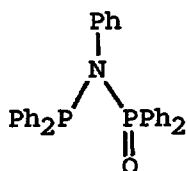
where A, B, C or D are selected from F, H, NO₂ and alkyl and E is endocyclic nitrogen or a C-CN group or isomers thereof, or

15 R = SiMe₃ or TiCl₂Cp where Me is methyl and Cp is cyclopentadiene

R₅ is aryl or alkyl, and

S* is S, Se, O or N-R, R being as defined hereinabove.

20 Amongst the exemplary ligands employed in W092/04118 are said to be those having the general formulae:-



25 The catalyst precursors described in W092/04118 are active as catalysts in the carbonylation reaction of methanol to form acetic acid and its derivatives such as methyl acetate. Whilst according to WO 92/04118 the process is said to be performable at 25°C to 200°C and the pressure is from 1 psig to 5000 psig, the preferred

30 conditions are said to be 50°C to 120°C and 40 to 400 psig and examples are only given at temperatures in the range 80-90°C and at a pressure of 40 psig.

The catalyst precursors described in W092/04118 are not entirely satisfactory.

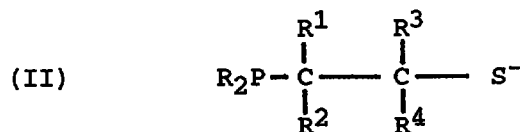
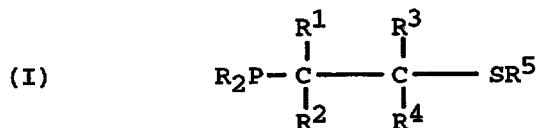
35 According to the present invention there is provided a process



for the liquid phase carbonylation of methanol or a reactive derivative thereof which process comprises contacting carbon monoxide with a liquid reaction composition comprising methanol or a reactive derivative thereof, a halogen promoter and a rhodium catalyst system comprising a rhodium component and a bidentate phosphorus-sulphur ligand, the ligand comprising a phosphorus dative centre linked to a sulphur dative or anionic centre by a substantially unreactive backbone structure comprising two connecting carbon atoms or a connecting carbon and a connecting phosphorus atom.

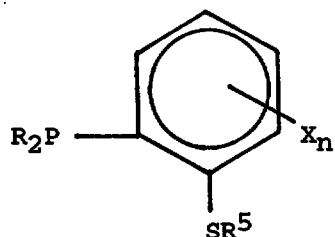
In one preferred embodiment, the phosphorus and sulphur dative centres or phosphorus dative centre and anionic sulphur centre are linked via two connecting carbon atoms in the backbone structure which backbone structure may comprise an unbranched hydrocarbyl group $-\text{CH}_2-\text{CH}_2-$, a branched hydrocarbyl group such as $(\text{CH}_3)\text{CHCH}_2$ or an unsaturated hydrocarbyl group such as a benzene ring (optionally substituted with a non-coordinating substituent such as $-\text{Si}(\text{CH}_3)_3$ or $-\text{CH}_3$) connected in the ortho-positions to the phosphorus and sulphur atoms of the ligand. Alternatively, the phosphorus and sulphur dative centres or the phosphorus dative centre and the anionic sulphur centre are linked via a connecting carbon and a connecting phosphorus atom in the backbone structure.

Preferably, the bidentate phosphorus-sulphur ligand has a general formula I, II, III, IV or V:



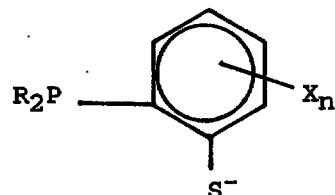


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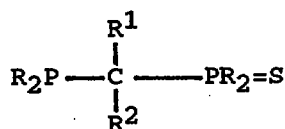
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(IV)



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(V)

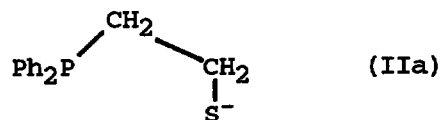
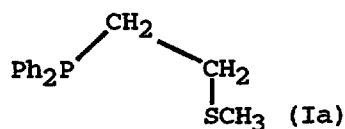


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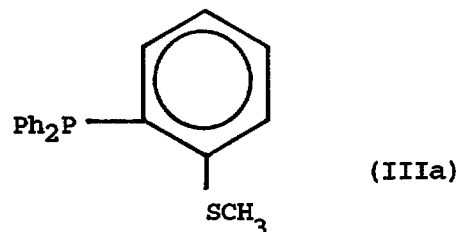
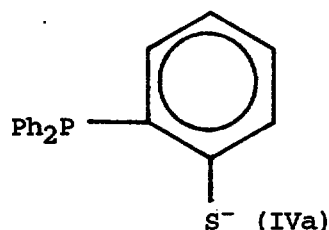
wherein the R groups are independently selected from C₁ to C₂₀ alkyl, cycloalkyl, aryl, substituted aryl and optionally substituted aralkyl; the R⁵ groups are selected from hydrogen, C₁ to C₂₀ alkyl, cycloalkyl, aryl, substituted aryl, acyl and optionally substituted aralkyl groups; the R¹ to R⁴ groups are independently selected from hydrogen, C₁ to C₂₀ alkyl and optionally substituted aralkyl; X is a non-coordinating substituent such as C₁ to C₂₀ alkyl, cycloalkyl, aryl, substituted aryl, C₁ to C₂₀ alkoxy, C₁ to C₂₀ alkylthio, trialkylsilyl or triarylsilyl, preferably, Si(CH₃)₃ or methyl and n is 0 to 4 preferably 0 or 1. Preferably, the R groups are independently selected from C₁ to C₈ alkyl, cyclohexyl, phenyl and optionally substituted aryl and the R⁵ groups are selected from C₁ to C₈ alkyl, cyclohexyl, phenyl, acetyl and benzyl. Preferably, the R¹ to R⁴ groups are independently selected from hydrogen or C₁ to C₈ alkyl. Preferably, when n=1, X is -Si(CH₃)₃ at the 6- position or X is -CH₃ at the 4- position.

Examples of preferred ligands are:

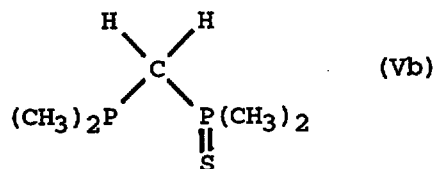
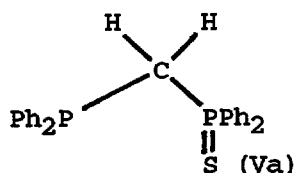
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wherein Ph is .

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In the process of the present invention, reactive derivatives of methanol include dimethyl ether, methyl acetate and methyl halide, for example, methyl iodide. The products of the process are methyl acetate and/or acetic acid. Preferably, the process according to the present invention is a process for the

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carbonylation of methanol or a reactive derivative thereof to produce acetic acid.

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The process of the present invention is suitably performed at a temperature in the range 25 to 250°C, preferably 50 to 250°C, more preferably 100 to 250°C, yet more preferably 135 to 250°C, and most preferably 145 to 200°C.

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The process of the present invention is suitably performed at a pressure in the range 10 to 200 barg, preferably 20 to 200 barg, more preferably 30 to 200 barg and most preferably 50 to 100 barg. Whilst the promotional effect is greatest at higher pressures, economic considerations may dictate the pressure to be used



industrially.

Acetic acid may be present as a solvent in the reaction composition in the process of the present invention.

5 Water may be present in the liquid reaction composition of the process of the present invention, for example, at a concentration in the range 0.1 to 20%, preferably 0.1 to 14% by weight based on the total weight of the liquid reaction composition. The water may be added to the liquid reaction composition and/or may be formed in situ by esterification of methanol with acetic acid solvent and/or
10 acetic acid reaction product present in the liquid reaction composition.

The rhodium component and bidentate phosphorus-sulphur ligand of the catalyst system may be added to the liquid reaction composition of the present invention in the form of a rhodium
15 complex in which the bidentate phosphorus-sulphur ligand is coordinated to rhodium. Preferably, a rhodium component having displaceable groups is pre-mixed with the bidentate phosphorus-sulphur ligand in a suitable inert solvent, for example methanol, prior to addition to the liquid reaction composition. For this
20 Rh^{III} components may not be suitable. With these provisos, the rhodium component may be added in any suitable form for example [Rh(CO)₂Cl]₂, [Rh(CO)₂I]₂, [Rh(Cod)Cl]₂, rhodium III chloride, rhodium III chloride trihydrate, rhodium III bromide, rhodium III iodide, rhodium III acetate, rhodium dicarbonylacetylacetonate,
25 RhCl(PPh₃)₃ and RhCl(CO)(PPh₃)₂.

The rhodium component of the catalyst system may be present in the liquid reaction composition, for example, at a concentration of 25 - 5000 ppm rhodium and the mole ratio of the rhodium component to the bidentate phosphorus-sulphur ligand is suitably in the range
30 1:0.5 to 1:4, preferably at a mole ratio of 1:1.

Preferably, the halogen promoter is an organic compound containing iodine, most preferably the halogen promoter is an alkyl iodide, preferably methyl iodide. The concentration of alkyl iodide in the liquid reaction composition is preferably in the range of 1
35 to 30% by weight, most preferably 5 to 20% by weight.



Also according to the present invention there is provided a rhodium complex having a formula $[\text{Rh}(\text{CO})\text{L}]_m$ or $[\text{Rh}(\text{CO})\text{LY}]$ wherein L is a bidentate phosphorus-sulphur ligand having a general formula, (II), (III), (IV) or (V) as hereinbefore defined, preferably (IIa), (IIIa), (IVa), (Va) or (Vb), Y is a halogen, preferably chlorine, bromine or iodine and m is less than 10, typically at least 2.

The invention will now be illustrated by reference to the following examples in which Ph-is  and Me-is CH_3 -

All preparations were carried out under an atmosphere of nitrogen using standard Schlenk-line techniques. Solvents were dried before use. Unless otherwise stated ligands were characterised by $^{31}\text{P}\{^1\text{H}\}$ nmr spectroscopy and complexes were characterised by $^{31}\text{P}\{^1\text{H}\}$ nmr, infrared spectroscopy and microanalysis. NMR spectra were recorded at ambient temperature on a JEOL EX270 spectrometer and were referenced to the ^2H lock signal from the solvent with $E_p = 40480740$ Hz (idealised value for 85% H_3PO_4): positive shifts are downfield. Infrared spectra were recorded on a Perkin-Elmer 1600 Series Fourier Transform spectrometer.

20 Preparation of Ligands

The ligand bis(diphenylphosphino)methane monosulphide $\text{Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2$ (Va) was prepared as described in Can. J. Chem., 1988, 66, 1272 by D E Berry, J Browning, K R Dixon and R W Hilt. The ligand 2-(diphenylphosphino)thiophenol 2-(Ph_2P) $\text{C}_6\text{H}_4(\text{SH})$ was prepared by the method of E Block, G Ofori-Okai and J Zubieta as described in J Am. Chem. Soc., 1989, 111, 2327 $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3): $\delta_p = -11.4$ ppm Diphenyl[2-(methylthio)phenyl]phosphine: $^{31}\text{P}\{^1\text{H}\}$ -NMR(CDCl_3): $\delta_p = -12.1$ ppm. The ligands $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(=\text{O})\text{Ph}_2$ and $\text{Ph}_2\text{PCH}_2\text{P}(=\text{O})\text{Ph}_2$ were prepared according to the method described in European patent application publication number 0072560. Triphenyl phosphine and $\text{P}(=\text{S})\text{Ph}_3$ are commercial materials which were obtained from Aldrich.

Preparation of Bis(dimethylphosphino)methane monosulphide

$\text{Me}_2\text{PCH}_2\text{P}(\text{S})\text{Me}_2$, (Vb)

A solution of elemental sulphur (0.848g, 26.5 mmol) in toluene



(70cm³) was added over a period of 5 minutes to a solution of bis(dimethylphosphino)methane (ex Strem; 3.6g, 26.5 mmol) in toluene (60cm³) at a temperature of 0°C. The resulting mixture was stirred for 30 minutes at 0°C and then for 1 hour at room temperature.

- 5 Solvent and unreacted bis(dimethylphosphino)methane were removed under reduced pressure to yield a white solid product (2.76g) comprising a mixture of Me₂PCH₂P(S)Me₂ (60% yield based on sulphur) and Me₂(S)PCH₂P(S)Me₂ (40% yield).

Preparation of Lithium 2-(diphenylphosphino)ethanethiolate

10 Ph₂PCH₂CH₂(SLi)

This preparation is adapted from the procedures described by J R Geigy FR 1401930 and J Chatt, J R Dilworth, J A Schmutz and J A Zubieta J. Chem. Soc. Dalton Trans., 1979 1595-99. To a solution of diphenylphosphine (ex Fluka; 0.134cm³, 0.144g, 0.772 mmol) in
15 diethyl ether (15cm³) was added butyllithium (0.31 cm³ of a 2.5 M solution in hexanes) and the solution was stirred for 30 minutes at room temperature. Ethylene sulphide (0.46 cm³, 0.109g, 0.772 mmol) was then added and the mixture was stirred for 2 hours at room temperature. The resulting ethereal solution of lithium 2-
20 (diphenylphosphino)ethanethiolate is suitable for preparing complexes of the 2-(diphenylphosphino)ethanethiolate anion without further treatment. 2-(Diphenylphosphino)ethanethiol: ³¹P{¹H}-NMR(CDCl₃): δ_P = -13.1 ppm. [2-(Methylthio)ethyl]diphenylphosphine: ³¹P{¹H}-NMR(CDCl₃): δ_P = -13.4 ppm.

25 Preparation of Rhodium Catalyst Systems

Preparation of [Rh(CO)LCl]₂; where L is Ph₂PCH₂P(S)Ph₂.{Va}

- To a solution of [Rh(CO)₂Cl]₂ (0.046g, 0.118 mmol) in methanol (1.9 cm³) was added a slurry of Ph₂PCH₂P(S)Ph₂ (0.099g, 0.237 mmol) in methanol (1.9 ml). Solvent was removed from the resulting
30 mixture under reduced pressure to give an orange solid of product (0.110g, 80% yield).

Reaction of [Rh(CO)₂Cl]₂ with Me₂PCH₂P(S)Me₂.{Vb}

- To a solution of [Rh(CO)₂Cl]₂ (0.092g, 0.237 mmol) in methanol (3.8 cm³) at a temperature of 0°C was added a solution of a mixture
35 of Me₂PCH₂P(S)Me₂ and Me₂(S)PCH₂P(S)Me₂ (0.132g, containing 0.474



mmol $\text{Me}_2\text{PCH}_2\text{P}(\text{S})\text{Me}_2$), prepared as described above, in methanol (3.8 cm^3). The resulting mixture (a yellow precipitate in methanol) was used directly as a catalyst for the carbonylation of methanol.

Preparation of Carbonylbis[(P,μ-S)-2-(diphenylphosphino)

- 5 benzenethiolatoldirhodium(I) Oligomer $\{[\text{Rh}(\text{CO})\text{L}]_n$: where L is 2-($\text{Ph}_2\text{P})\text{C}_6\text{H}_4(\text{S}^-)$), IVa}

- A mixture of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.15g, 0.385 mmol), 2-(diphenylphosphino)thiophenol (0.22g, 0.747 mmol) and MeOLi (0.07g, 1.6 mmol) in methanol (25 cm^3) was refluxed for 30 minutes. The
10 resulting red-orange precipitate of product was recovered by filtration (0.287g, 88% yield). It is now preferred to stir the reagents together for 30 minutes at room temperature instead of refluxing. $\text{C}_{19}\text{H}_{14}\text{OPRhS } M_r = 424.26$. Calcd. C 53.79%, H 3.33%; Found C 53.66%, H 3.43%. $^{31}\text{P}\{^1\text{H}\}$ -NMR (acetone- d_6): $\delta_p = +60.5 \text{ ppm}$ ($d, ^1J_{\text{PRh}} = 158 \text{ Hz}$). $\nu(\text{C}=\text{O}) = 1946 \text{ cm}^{-1}$ (Nujol mull).

Preparation of Carbonylbis[(P,μ-S)-2-(diphenylphosphino)

ethanethiolatoldirhodium(I) Oligomer $\{[\text{Rh}(\text{CO})\text{L}]_n$: where L is $\text{Ph}_2\text{PCH}_2\text{CH}_2(\text{S}^-)$), IIa}

- To a solution of lithium 2-(diphenylphosphino)ethanethiolate
20 (prepared as described above) was added a solution of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.15g, 0.386 mmol) in methanol (10 cm^3) and the resulting mixture was stirred for 30 minutes. An orange precipitate of product was recovered by filtration (0.264g, 91% yield). $\text{C}_{15}\text{H}_{14}\text{OPRhS } M_r = 376.22$. Calcd. C 47.89%, H 3.75%; Found C 48.01%, H 3.49%. $^{31}\text{P}\{^1\text{H}\}$ -
25 NMR (acetone- d_6): $\delta_p = +63.7 \text{ ppm}$ ($d, ^1J_{\text{PRh}} = 158 \text{ Hz}$) $\nu(\text{C}=\text{O}) = 1947 \text{ cm}^{-1}$ (Nujol mull).

Preparation of Chlorocarbonyl[(P,S)-diphenyl(2-(methylthio)phenyl)phosphine]rhodium(I) $\{[\text{Rh}(\text{CO})\text{LCl}]\}$: where L is 2-($\text{Ph}_2\text{P})\text{C}_6\text{H}_4(\text{SMe})$), IIIa}

- 30 To a solution of 2-(diphenylphosphino)thiophenol (0.227g, 0.772 mmol) in methanol (25 cm^3), at a temperature of -20°C , was added dropwise iodomethane (0.048 cm^3 , 0.109g, 0.772 mmol) over a period of 15 minutes. The solution was allowed to warm to room temperature and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.15g, 0.386 mmol) in methanol (10
35 cm^3) was added. The mixture was stirred for 2 hours and a dark



brown precipitate of product was recovered by filtration (0.179g, 49% yield). $C_{20}H_{17}ClOPRhS$ $M_r = 474.75$. Calcd. C 50.60%, H 3.61%: Found C 50.88%, H 3.72%. $^{31}P\{^1H\}$ -NMR ($CDCl_3$): $\delta_p = +70.3$ ppm ($d, ^1J_{PRh} = 158$ Hz) $\nu(C=O) = 1998$ cm^{-1} (Nujol mull)

5 Preparation of Chlorocarbonyl[(P, S)-(2-(methythio)ethyl)diphenylphosphine]rhodium(I) ([Rh(CO)LCI]; where L is $Ph_2PCH_2CH_2(SMe)_2$)]

To a solution of lithium 2-(diphenylphosphino)ethanethiolate (prepared as described above) was added dropwise iodomethane (0.048 cm^3 , 0.109 g, 0.772 mmol) and the mixture was stirred for 2 hours. To this mixture was added a solution of $[Rh(CO)_2Cl]_2$ (0.15 g, 0.386 mmol) in methanol (15 cm^3) and the mixture was stirred for a further 30 minutes. A dark brown precipitate of product was recovered by filtration (0.191 g, 58% yield). $C_{16}H_{17}ClOPRhS$ $M_r = 426.71$. Calcd. C 45.04%, H 4.02%: Found C 44.26%, H 3.61%. $^{31}P\{^1H\}$ -NMR ($CDCl_3$): $\delta_p = +72.7$ ppm ($d, ^1J_{PRh} = 162$ Hz). $\nu(C=O) = 1984$ cm^{-1} (Nujol mull)

15 General Procedure for Carbonylation of Methanol

Methanol (22.69g), acetic acid (59.79g) and methyl iodide (6.84g) were charged to a 150 cm^3 Hastelloy B2 autoclave which was equipped with a Magnedrive (TM) stirrer. The autoclave was then flushed twice with nitrogen and once with carbon monoxide. The reaction mixture was heated under an initial pressure of 1 bara of carbon monoxide to the desired reaction temperature by means of electrical heating coils. The temperature of the reaction mixture was maintained to within $1^\circ C$ of the desired reaction temperature by careful control of the amount of heat supplied by the electrical heating coils. A rapid and consistent rate of stirring (1000 rpm) was employed. In a first series of experiments a ligand (1.89×10^{-3} moles) and $[Rh(CO)_2Cl]_2$ (0.092g; 2.37×10^{-4} moles) were partially or wholly dissolved in methanol (5g) (see Tables 1 and 2) and the solution or slurry, as the case may be, was injected into the autoclave as the autoclave was simultaneously pressurised with carbon monoxide to a total pressure of 70 barg. In a second series of experiments of rhodium complex (see Table 3) was injected as a solution or slurry in methanol (5g) into the autoclave as the



autoclave was simultaneously pressurised with carbon monoxide to a total pressure of 70 barg. In both series of experiments the pressure in the autoclave was maintained by uptake of carbon monoxide from a ballast vessel and the carbonylation rate was determined by measuring the rate of uptake of carbon monoxide from the ballast vessel. At the end of the reaction, as monitored by uptake of carbon monoxide, the reaction mixture was cooled, the autoclave was vented and a sample of the reaction mixture was analysed by gas chromatography which confirmed the formation of acetic acid during the reaction. The results of carbonylation using different ligands are given in Tables 1 to 3.

TABLE 1
REACTION RATES AT 185°C

Experiment	Ligand	Rate ^a mol/l/h
Experiment A	-	2.3
Experiment B	PPh ₃	2.6
Experiment C	P(=S)Ph ₃ ^b	3.5
Experiment D	Ph ₂ PCH ₂ CH ₂ P(=O)Ph ₂	2.7
Experiment E	Ph ₂ PCH ₂ P(=O)Ph ₂	3.0
Example 1	Ph ₂ PCH ₂ P(=S)Ph ₂ (Va)	14.2

- (a) The rate is the average rate up to the point at which half of the methanol has been converted to acetic acid.
- (b) Ph(=S)Ph₃ was included in the initial autoclave charge and was not present in the solution which was injected into the autoclave.

The results given in Table 1 show that at a temperature of 185°C the rate of carbonylation of methanol in the presence of triphenylphosphine (a tertiary phosphine ligand; Experiment B) was only marginally higher than the rate in the absence of a phosphine ligand (Experiment A). An improvement in rate was observed in the presence of the monodentate tertiary phosphine sulphide ligand P(=S)PPh₃ which was employed in Experiment C. This ligand was also superior in performance to the tertiary bisphosphine monoxide ligands used in Experiments D and E. However, the reaction rate



obtained according to the present invention in the presence of $\text{Ph}_2\text{PCH}_2\text{P}(=\text{S})\text{Ph}_2$ (a tertiary bisphosphine monosulphide ligand (Example 1)) was 6.2 times that obtained in the absence of a phosphine ligand (Experiment A) and 4.1 times that obtained using the monodentate tertiary phosphine sulphide ligand of Experiment C. Moreover, the carbonylation rate obtained in Example 1 was 4.7 times higher than that obtained in the presence of the corresponding monoxide ligand $\text{Ph}_2\text{PCH}_2\text{P}(=\text{O})\text{Ph}_2$ (Experiment E).

Table 2

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Reaction Rates at 150°C

Example	Ligand	Rate ^a mol/l/h
Experiment F	$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(=\text{O})\text{Ph}_2$	0.6
Example 2	$\text{Ph}_2\text{PCH}_2\text{P}(=\text{S})\text{Ph}_2$ (Va)	7.6

(a) The rate is the average rate up to the point at which half of the methanol has been converted to acetic acid.

The results given in Table 2 show that at a temperature of 150°C the carbonylation rate in the presence of $\text{Ph}_2\text{PCH}_2\text{P}(=\text{S})\text{Ph}_2$ is 12.7 times that obtained using the monoxide ligand $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(=\text{O})\text{Ph}_2$.

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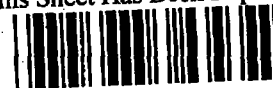
Table 3

Reaction Rates at 185°C

Experiment	Complex of Rhodium Component and Ligand	Moles of Complex ($\times 10^4$)	Ligand, L	Rate mol/l/h
Example 3	$[\text{Rh}(\text{CO})\text{LCl}]$	4.74	$\text{Ph}_2\text{PCH}_2\text{P}(\text{S})\text{Ph}_2$ (Va)	19.6a
Example 4	$[\text{Rh}(\text{CO})_2\text{Cl}]_2/2\text{L}^c$	2.37 (d)	$\text{Me}_2\text{PCH}_2\text{P}(\text{S})\text{Me}_2$ (Vb)	12.7b
Example 5	$[\text{Rh}(\text{CO})\text{L}]_m$	4.74/m (d)	$2-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4(\text{S}^-)$ (IVa)	6.2a
Example 6	$[\text{Rh}(\text{CO})\text{L}]_m$	4.74/m (d)	$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{S}^-$ (IIa)	8.9a
Example 7	$[\text{Rh}(\text{CO})\text{LCl}]$	3.38	$2-(\text{Ph}_2\text{P})\text{C}_6\text{H}_4(\text{SMe})$ (IIIa)	4.2a
Example 8	$[\text{Rh}(\text{CO})\text{LCl}]$	3.17	$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SMe}$ (Ia)	4.5a
Experiment A	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	2.37 (d)	-	2.3a

- (a) The rate is the average rate up to the point at which half of the methanol has been converted to acetic acid.
- (b) Initial rate.
- (c) Resulting complex was not characterised.
- (d) Mole of rhodium = 4.74×10^{-4} .





The results given in Table 3 show that at a temperature of 185°C, when a rhodium complex having a bidentate phosphorus-sulphur ligand co-ordinated to rhodium is charged to the autoclave (Examples 3 to 8) the rate of carbonylation of methanol is significantly higher than for Experiment A where $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ without a bidentate phosphorus-sulphur ligand was charged to the autoclave.

Experiment G

A carbonylation experiment was performed using the same procedure as for the experiments in Table 3 but using 0.474 mmol of $[\text{Rh}(\text{CO})\text{LCl}]$ wherein L is $\text{Ph}_2\text{PN}(\text{Ph})\text{P}(\text{S})\text{Ph}_2$. Thus, to a solution of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.092g, 0.237mmol) in methanol (3.8cm^3) was added a slurry of $\text{Ph}_2\text{PN}(\text{Ph})\text{P}(\text{S})\text{Ph}_2$ (0.233g, 0.473mmol) in methanol (3.8cm^3). The ligand $\text{Ph}_2\text{PN}(\text{Ph})\text{P}(\text{S})\text{Ph}_2$ was prepared by the procedure described by MS Balakrishna et al in Inorg. Chem. 1993 vol 32 5676-5681.

The resulting yellow slurry of $[\text{RhCl}(\text{CO})\text{PPh}_2\text{N}(\text{Ph})\text{P}(\text{S})\text{Ph}_2]$ formed in the methanol over 5 minutes and was used directly as the catalyst charge in the carbonylation experiment. In the carbonylation experiment, the carbonylation rate (average rate up to the point at which half of the methanol had been converted to acetic acid was 3.4 mol/l/hr which is less than the rates for the ligands according to the present invention in Table 3. The use of $\text{Ph}_2\text{PN}(\text{Ph})\text{P}(\text{S})\text{Ph}_2$ in a carbonylation reaction is described in WO 92/04118. This is not an example according to the present invention.

Examples 9-11

Example 3 was repeated at different pressures and the results are shown in Table 4.



Table 4
Reaction Rates at Different Pressures

Example	Pressure (barg)	Reaction Rate (mol/l/hr) ^a
9	30	14.0
10	50	21.2
3	70	19.6
11	100	19.8

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(a) The rate is the average rate up to the point at which half of the methanol has been converted to acetic acid.

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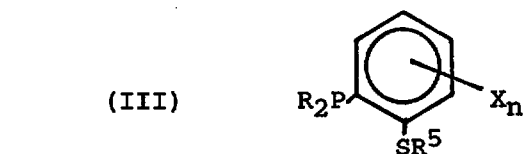
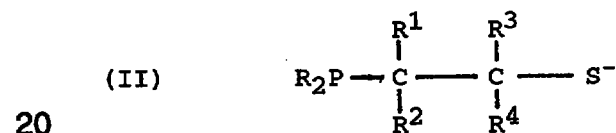
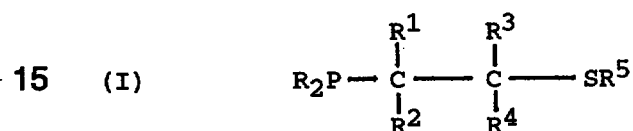
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Case 8329/8405 cog (2)

Claims:

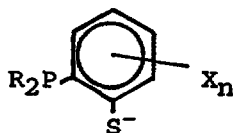
1. A process for the liquid phase carbonylation of methanol or a reactive derivative thereof which process comprises contacting carbon monoxide with a liquid reaction composition comprising methanol or a reactive derivative thereof, a halogen promoter and a rhodium catalyst system comprising a rhodium component and a bidentate phosphorus-sulphur ligand, the ligand comprising a phosphorus dative centre linked to a sulphur dative or anionic centre by a substantially unreactive backbone structure comprising two connecting carbon atoms or a connecting carbon and a connecting phosphorus atom.
2. A process as claimed in claim 1 in which the bidentate phosphorus-sulphur ligand is selected from the group consisting of:-



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(IV)

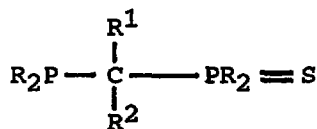


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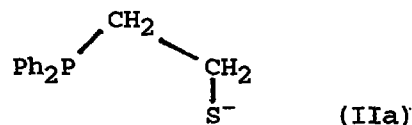
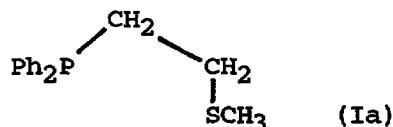
(V)



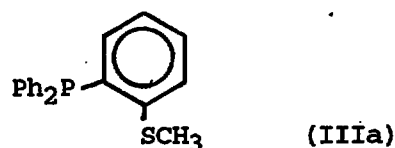
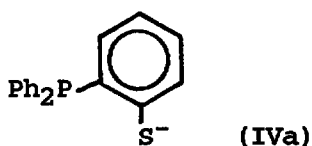
- wherein the R groups are independently selected from the group consisting of C₁ to C₂₀ alkyl, cycloalkyl, aryl, substituted aryl and optionally substituted aralkyl; the R⁵ groups are selected from the group consisting of hydrogen, C₁ to C₂₀ alkyl, cycloalkyl, aryl, substituted aryl, acyl and optionally substituted aralkyl groups; the R¹ to R⁴ groups are independently selected from the group consisting of hydrogen, C₁ to C₂₀ alkyl and optionally substituted aralkyl; X is a non-coordinating substituent and n is 0 to 4.

3. A process as claimed in claim 2 in which the R groups are independently selected from the group consisting of C₁ to C₈ alkyl, cyclohexyl, phenyl and optionally substituted aryl.
4. A process as claimed in claim 2 or claim 3 in which the R⁵ groups are selected from the group consisting of hydrogen, C₁ to C₈ alkyl, cyclohexyl, phenyl, acetyl and benzyl.
5. A process as claimed in any one of claims 2 to 4 in which the R¹ to R⁴ groups are independently selected from the group consisting of hydrogen and C₁ to C₈ alkyl.
6. A process as claimed in any one of claims 2 to 5 in which X is Si(CH₃)₃ or methyl.
7. A process as claimed in claim 2 in which the bidentate-sulphur ligand is selected from the group consisting of:-

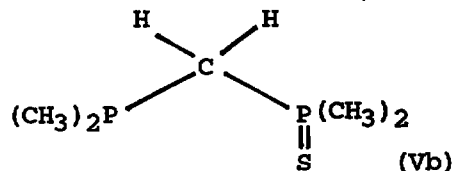
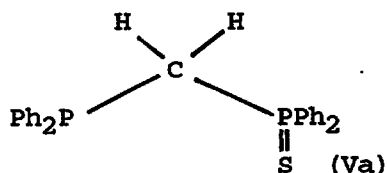
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wherein Ph is

8. A process as claimed in any one of the preceding claims in which the mole ratio of the rhodium component to the bidentate phosphorus-sulphur ligand is in the range 1:0.5 to 1:4.
- 15 9. A process as claimed in any one of the preceding claims in which the process is performed at a temperature in the range of 25 to 250°C and at a pressure in the range 10 to 200 barg.
10. A process as claimed in any one of the preceding claims in which the liquid reaction composition comprises water at a
- 20 concentration in the range of 0.1 to 20% by weight, an alkyl iodide at a concentration in the range 1 to 30% by weight and a rhodium component at a concentration in the range 25 - 5000 ppm.
11. A process as claimed in any one of the preceding claims in which the carbonylation product is acetic acid.
- 25 12. A catalyst system consisting of a rhodium component and a bidentate phosphorus-sulphur ligand in which the ligand is selected from the group consisting of II, III, IV and V as defined in any one of claims 2 to 6.
13. A catalyst system as claimed in claim 12 in which the
- 30 bidentate phosphorus-sulphur ligand is selected from the group consisting of IIa, IIIa, IVa, Va and Vb as defined in claim 7.
14. A catalyst system as claimed in claim 12 or claim 13 in which the mole ratio of the rhodium component to the bidentate phosphorus-sulphur ligand is in the range 1:0.5 to 1:4.
- 35 15. A rhodium complex of formula $[\text{Rh}(\text{CO})\text{L}]_m$ or $[\text{Rh}(\text{CO})\text{LY}]$ in which



L is selected from the group of bidentate phosphorus-sulphur ligands consisting of II, III, IV and V, as defined in claim 2, Y is a halogen and m is a number less than 10.

- 5 16. A rhodium complex as claimed in claim 15 in which L is selected from the group of bidentate phosphorus-sulphur ligands consisting of IIa, IIIa, IVa, Va and Vb as defined in claim 7 and m is at least 2.

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