P/00/001 2/5/91
Section 29

AUSTRALIA

Patents Act 1990

PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

We, being the persons identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

[71] Applicant: HOECHST AKTIENGESELLSCHAFT

Address: D-65926 FRANKFURT AM MAIN, FEDERAL REPUBLIC OF GERMANY

[70] Nominated Person: HOECHST AKTIENGESELLSCHAFT

Address: D-65926 FRANKFURT AM MAIN, FEDERAL REPUBLIC OF GERMANY

[54] Invention Title: PROCESS FOR PREPARING ALDEHYDES

[72] Name(s) of actual inventor(s): WOLFGANG A. HERRMANN, MARTINA ELISON, JAKOB FISCHER and CHRISTIAN KOCHER

[74] Address for service in Australia: c/o WATERMARK PATENT & TRADEMARK ATTORNEYS, of
290 Burwood Road, Hawthorn, Victoria 3122, Australia
Attorney Code: WM

BASIC CONVENTION APPLICATION(S) DETAILS

[31] Application Number	[33] Country	Country Code	[32] Date of Application
P44 47 067.3	GERMANY	DE	29 DECEMBER 1994

Basic Applicant(s): HOECHST AKTIENGESELLSCHAFT

Drawing number recommended to accompany the abstract ....

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

....

Carolyn J. Harris
Registered Patent Attorney

DATED this 28th day of December 1995.

P/00/008b 12/11/91
Section 29 (1)
Regulation 3.1 (2)

694819

AUSTRALIA

Patents Act 1990

NOTICE OF ENTITLEMENT

We, **HOECHST AKTIENGESELLSCHAFT** of, D-65926 Frankfurt AM Main, Federal Republic of Germany, being the applicant in respect of Application No. 40705/95 state the following:-

The Person nominated for the grant of the patent has entitlement from the actual inventors by virtue of German Inventorship Law.

The person nominated for the grant of the patent is the applicant of the basic application listed on the patent request form.

The basic application listed on the request form is the first application made in a Convention country in respect of the invention.

HOECHST AKTIENGESELLSCHAFT
By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

Karen J. Sinclair
Registered Patent Attorney

29 May 1998

AU9540705

(12) PATENT ABRIDGMENT (11) Document No. AU-B-40705/95
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 694819

(Modified Examination)

(54) Title
PROCESS FOR PREPARING ALDEHYDES

International Patent Classification(s)
(51)^6 **C07C 045/50**

(21) Application No. : **40705/95** (22) Application Date : **28.12.95**

(30) Priority Data

(31) Number **4447067** (32) Date **29.12.94** (33) Country **DE GERMANY**

(43) Publication Date : **04.07.96**

(44) Publication Date of Accepted Application : **30.07.98**

(71) Applicant(s)
HOECHST AKTIENGESELLSCHAFT

(72) Inventor(s)
WOLFGANG A. HERRMANN; MARTINA ELISON; JAKOB FISCHER; CHRISTIAN KOCHER

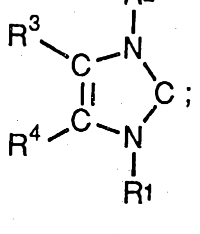
(74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122

(57) Claim

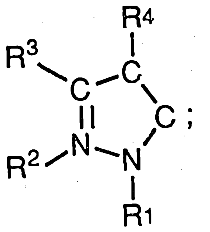
1. A process for preparing aldehydes by reaction of a compound selected from the group consisting of monoolefins, polyolefins, cycloolefins, or derivatives thereof with carbon monoxide and hydrogen at temperatures of from 20° to 180° C. and pressures of from 0.1 to 30 MPa in the presence of complexes of cobalt or of rhodium as a catalyst, wherein said complexes are of the formula

$$[L_a M_b X_c]^n (A)_n, \qquad (I)$$

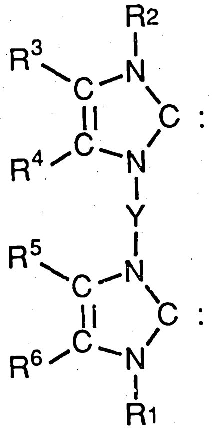
wherein M is cobalt or rhodium as a central atom, X's are individually monodentate or multidentate, charged or uncharged ligands bound to said central atom and L's are individually ligands bound to said central atom and are selected from the group consisting of monocarbenes and dicarbenes of the formulas



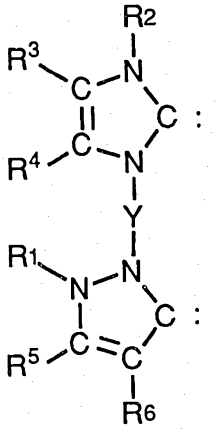
(II)



(III)



(IV)



(V)

wherein R^1, R^2, R^3, R^4, R^5, and R^6 are individually selected from the group consisting of straight or branched chain, sulfonated or unsulfonated alkyls having 1 to 7 carbon atoms; sulfonated or unsulfonated aliphatic monocyclics and polycyclics having 5 to 18 carbon atoms; sulfonated or unsulfonated alkenyls having 2 to 5 carbon atoms; sulfonated or unsulfonated aryls having 6 to 14 carbon atoms; and sulfonated or unsulfonated aralkyls having 7 to 19 carbon atoms; R^1 and R^2 are also selected from the group consisting of $-(CH_2)_mPR_2$, wherein m=1, 2, 3 or 4 and R=benzyl, phenyl, substituted phenyl, naphthyl; $-(CH_2)_mNR'_2$ (wherein R'=alkyl, vinyl, allyl, benzyl, and aryl); and $-(CH_2)_mOR''$ (wherein R''=alkyl); R^3, R^4 R^5 and R^6 can also be hydrogen; R^3

.../3

together with R^4, and R^5 together with R^6, may individually form fused and sulfonated or unsulfonated radicals having 3 to 7 carbon atoms, R^1, R^2, R^4, or R^6, together with X may form a ring, Y is selected from the group consisting of saturated or unsaturated, straight or branched chain alkylidenes having 1 to 4 carbon atoms, dialkylsilylenes, and tetraalkyldisilylenes; A is a singly charged anion or the chemical equivalent of a multiply charged anion, b is an integer from 1 to 3, a is an integer from 1 to 4 times b, and c=0 or an integer from 1 to 4 times b, and n' =0 or an integer from 1 to 6.

P/00/011 28/5/91
Regulation 3.2(2)

AUSTRALIA

Patents Act 1990

ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Application Number:
Lodged:

Invention Title: PROCESS FOR PREPARING ALDEHYDES

The following statement is a full description of this invention, including the best method of performing it known to us :-

Process for preparing aldehydes

The invention relates to a process for preparing aldehydes by hydroformylation of olefins in the presence of complexes of cobalt or of rhodium which contain heterocyclic carbenes as ligands. The reaction of olefins with carbon monoxide and hydrogen can be carried out either in a homogeneous or in a heterogeneous phase.

It is known that reaction of olefins with carbon monoxide and hydrogen (hydroformylation) can be used to prepare aldehydes and alcohols which contain one carbon atom more than the starting olefin. The reaction is catalyzed by hydrido-metal carbonyls, preferably of the metals of groups 8, 9, 10 of the Periodic Table (corresponding to the IUPAC recommendation of 1985). Apart from cobalt which was originally used as catalyst metal and has been widely used in industry, rhodium has recently been gaining increasing importance. In contrast to cobalt, rhodium allows the reaction to be carried out at low pressure. In addition, terminal olefins preferentially form n-aldehydes and only subordinate amounts of iso-aldehydes. Finally, the hydrogenation of the olefins to give saturated hydrocarbons is also significantly lower in the presence of rhodium catalysts than when using cobalt catalysts. In the processes introduced in industry, the rhodium catalyst is used in the form of modified hydrido-rhodium carbonyls which contain additional ligands, in particular teriary, organic phosphines or phosphites. The cobalt catalysts too are used in the form of carbonyls which additionally contain phosphines or phosphites as ligands, even though this variant of the hydroformylation is of lesser industrial importance than processes in which rhodium serves as catalyst.

The ligands by means of which the activity of the catalyst metal used is controlled (therefore also referred to as control ligands) are usually present in excess over the amount required for formation of the complex and thereby stabilize the complex in the sense of the law of mass action. The catalyst system therefore comprises a complex and free ligand, and the ligand is important not only for the specific catalytic activity, but also for the stability of the complex.

The hydroformylation reaction can be carried out either in homogeneous or in heterogeneous systems. In the homogeneously catalyzed reaction, the catalyst is homogeneously dissolved in the reaction product and a solvent which may also be present. This procedure has proved itself well both when using cobalt catalysts or when using rhodium catalysts. However, difficulties are presented in the separation of the reaction products and, in the case of the reaction catalyzed by rhodium, in the recovery of the catalyst. Product and catalyst solution are customarily separated from one another by distillation. However, owing to the thermal sensitivity of the aldehydes and alcohols formed, this route can only be used in the hydroformylation of lower olefins, i.e. olefins having up to about 8 carbon atoms in the molecule.

The indicated deficiencies are avoided in the rhodium-catalyzed reaction by using water-soluble rhodium complexes as catalysts. Such a process is described, for example, in DE-C 26 27 354. The solubility of the rhodium complexes is here achieved by use of sulfonated triarylphosphines as constituents of the complexes. In this process embodiment, the separation of the catalyst from the reaction product after the reaction is complete is carried out simply by separation of aqueous and organic phases, i.e. without distillation and thus without additional thermal process steps. A further feature of this procedure is that n-aldehydes are formed with particularly high selectivity from terminal olefins and iso-aldehydes are formed only in very subordinate amounts. The complexing constituents used for water-soluble rhodium complexes are preferably sulfonated triarylphosphines and additionally carboxylated triarylphosphines.

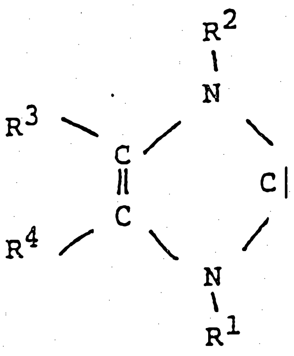
Organic phosphines, regardless of whether they are soluble in organic media or in water, have proven themselves well in industrial practice as control ligands owing to their wide variety, their catalytic activity and their selectivity. Nevertheless, a series of disadvantages stand in the way of their wider use. These include, in particular, the oxidation sensitivity which occurs especially in the presence of metals and metal ions. Therefore, when using catalysts based on phosphine-containing complexes, measures have to be taken to exclude oxidizing agents such as oxygen or air so as to reduce the losses of the ligands, which can frequently only be prepared at high cost. A further property which all organic phosphines have in common and which limits their possible uses is the irreversible cleavage of phosphorus-carbon bonds which, for example in the hydroformylation, occurs to an increased extent above certain temperatures dependent on the type of phosphine and which leads to deactivation of the catalyst and thus to high phosphine consumption which impairs the economics. Finally, the conventional alkylphosphines and arylphosphines, like the organic phosphites similarly used as ligands, do not allow coverage of the entire range of the electronic control possibilities in respect of the catalytically active metal centers. In particular, there is a lack of strongly nucleophilic electron-rich ligands which are resistant to oxidizing agents and form a stable bond to the metal.

It is therefore an object of the invention to develop new metal complexes as catalysts for the hydroformylation reaction, which metal complexes do not have the indicated disadvantages and, in addition, can be easily and inexpensively synthesized. Further, the constitution of the control ligands should be able to be altered in a simple manner so that it is possible to prepare catalysts which can be matched to individual catalytic problems.

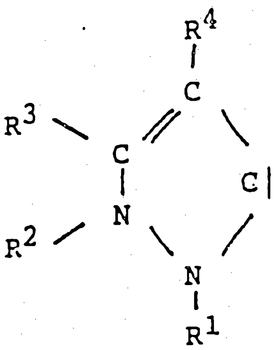
This object is achieved by a process for preparing aldehydes by reaction of monoolefins, polyolefins, cycloolefins or derivatives of these classes of compounds with carbon monoxide and hydrogen at temperatures of from 20 to 180°C and pressures of from 0.1 to 30 MPa in the presence of complexes of cobalt or of rhodium as catalyst. In the process, the complexes have the formula

$$[L_aM_bX_c]^n(A)_n,$$

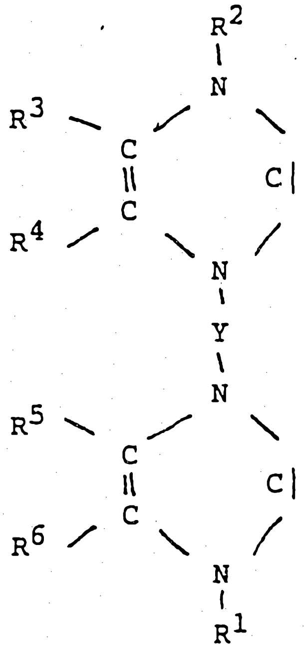
where M is cobalt or rhodium as central atom, X are monodentate or multidentate, charged or uncharged ligands bound to the central atom and L are likewise ligands bound to the central atom M which are monocarbenes of the formulae


(II)

and

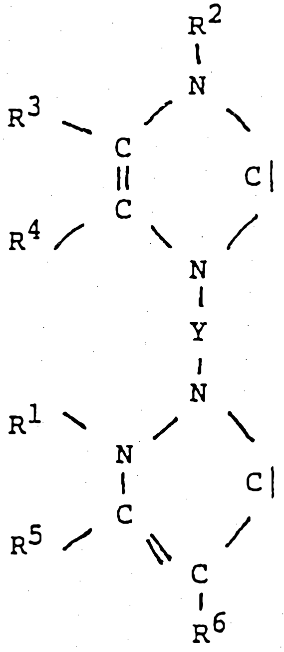

(III)

or dicarbenes of the formulae



(IV)

and



(V)

,

where R^1, R^2, R^3, R^4, R^5 and R^6 are identical or different, straight-chain or branched, sulfonated or unsulfonated alkyl radicals having from 1 to 7 carbon atoms, sulfonated or unsulfonated aliphatic monocyclic or polycyclic radicals having from 5 to 18 carbon atoms, sulfonated or unsulfonated alkenyl radicals having from 2 to 5 carbon atoms, sulfonated or unsulfonated aryl radicals having from 6 to 14 carbon atoms or sulfonated or unsulfonated aralkyl radicals having from 7 to 19 carbon atoms, R^1 and/or R^2 can also be $-(CH_2)_mPR_2$, where m = 1, 2, 3 or 4 and R = benzyl, phenyl, substituted phenyl, naphthyl, furthermore $-(CH_2)_mNR'_2$ where m is as defined above and R' = alkyl, vinyl, allyl, benzyl and aryl, and also $-(CH_2)_mOR''$ where m is as defined above and R" = alkyl, in particular methyl, vinyl, allyl, benzyl or phenyl; R^3, R^4, R^5 and R^6 can also be hydrogen, R^3 together with R^4 and R^5 together with R^6 can in each case also be identical or different fused and sulfonated or unsulfonated radicals having from 3 to 7 carbon atoms, R^1, R^2, R^4 or R^6 together with ligand X can form a ring, Y is a saturated or unsaturated, straight-chain or branched alkylidene radical having from 1 to 4 carbon atoms or a dialkylsilylene radical or tetraalkyldisilylene radical, A is a singly charged anion or the chemical equivalent of a multiply charged anion, b is an integer from 1 to 3, a is an integer from 1 to 4 times b, c = 0 or an integer from 1 to 4 times b and n = 0 or an integer from 1 to 6.

DETAILED DESCRIPTION OF THE INVENTION

X is a monodentate or multidentate ligand which can be present in the complexes, in addition to the carbenes, selected from the group consisting of hydrogen, hydrogen ion, halogens, halide ions, pseudohalides, carboxylate ions, sulfonate ions, alkyls having 1 to 7 carbon atoms, amides, alkoxides, acetylacetonates, carbon monoxide, nitrogen monoxide, nitriles, isonitriles, monoolefins, diolefins, alkynes, and π-aromatic radicals. If a plurality of these ligands is present in the molecule of the complex, they can be the same or different.

In the monocarbenes or dicarbenes corresponding to Formulas (II), (III), (IV) and (V) which are derived from imidazole and from pyrazole or their derivatives, R^1 to R^6 are desirably methyl, isopropyl, tert-butyl, benzyl, triphenylmethyl, phenyl, tolyl, xylyl, mesityl and/or adamantyl. R^1 and R^2 are preferably methyl, tert-butyl, phenyl, benzyl and/or o-tolyl; R^3 and R^4 are preferably hydrogen and/or methyl.

R^3 and R^4 and R^5 and R^6 can, together with two adjacent carbon atoms of the imidazole ring or the C—N moiety in the pyrazole ring, form a ring system. R^3 and R^4 or R^5 and R^6 are then preferably the moieties $(CH)_4$ thus leading to the formation of a fused aromatic six-membered ring; $(CH_2)_4$; and $(CH_2)_5$.

The bridges denoted by Y are preferably methylene, dimethyl-methylene, diphenylmethylene, 1,3-phenylene and ethylidene groups. Among the silicon-containing bridges, the dimethylsilylene and the tetramethyldisilylene groups are preferred.

a is preferably 1 or 2, b is preferably 1; n is in particular a number from 0 to 3.

A is preferably a halide, pseudohalide, tetraphenylborate, tetrafluoroborate, hexafluorophosphate and carboxylate ion, among the latter particularly the acetate ion, furthermore a metal complex anion such as, for example, tetracarbonylcobaltate, hexafluoroferrate(III), tetrachloroferrate, tetrachloroaluminate or tetrachloropalladate(II).

The cobalt and rhodium complexes used as catalysts can be obtained by various routes. One preparative method starts out from simple compounds, i.e. salts or metal complexes (such as the acetylacetonates, metal carbonyls), of each element which forms the central atom of the complex. According to another variant, the new compounds are obtained from complexes by ligand exchange or by elimination and/or substitution reactions, for example from usual solvent complexes of these metal compounds. The compounds claimed can also be obtained by simple addition of the carbene to the respective metal component, with this molecular addition also being able to occur with breaking up of a bridge structure.

The carbenes are used, depending on their stability, either in free form as solution or, more frequently, prepared in the reaction mixture from compounds which can be converted into carbenes under the reaction conditions. The most important method of formation is the deprotonation of imidazolium or pyrazolium salts, if desired by addition of bases such as metal hydrides, carbonylmetallates, metal carboxylates, metal alkoxides or metal amides.

The reaction of the starting materials, i.e. the simple salts or the complexes, with the carbenes and, if desired, further ligands is carried out by mixing the reactants in a solvent at room temperature or elevated temperature. The reaction proceeds rapidly and is often essentially complete after a few minutes. However, to complete the reaction, it is advisable to employ reaction times of up to a number of hours, particularly when the starting materials are only partially dissolved in the medium used, i.e. they react from suspension.

To prepare water-soluble complexes containing sulfonated ligands, the starting materials used include at least one reactant whose molecule or molecular fragment is sulfonated.

To isolate the new complexes from the reaction medium, it has been found to be useful to remove the solvent, advantageously in a high vacuum. The crude product is purified by washing and recrystallization from a suitable solvent or solvent mixture which can be determined in the individual case by preliminary experiments.

The cobalt and rhodium complexes used according to the invention as catalysts for the hydroformylation reaction are soluble in organic solvents, as salts also in water, particularly when they contain aliphatic or aromatic radicals substituted by sulfonic acid groups. They are very thermally stable and frequently stable even at temperatures above 350°C. In addition, it is notable that they hardly undergo oxidation reactions, in contrast to phosphines and phosphites. Finally, the complexes do not tend to dissociate. It is therefore frequently not necessary to use the ligands for controlling catalyst activity and stability in an excess over the stoichiometric amount required for formation of the complex. If it is found to be advantageous to use an excess of ligand, this can be significantly lower than when using phosphines or phosphites.

Depending on their solubility, the catalytically active complexes of cobalt or rhodium can be used homogeneously dissolved in the organic reaction medium which usually comprises the starting olefin, the reaction product, reaction byproducts and possibly a solvent. They can also be used as a separate phase in aqueous solution in a heterogeneous reaction system. Particularly suitable water-soluble catalysts are complexes containing heterogeneous carbene ligands substituted by sulfonic acid groups.

The cobalt or rhodium complexes are generally synthesized prior to the actual reaction, but they can also be prepared in situ in the reaction mixture of the hydroformylation. In both cases, the catalysts are obtained as described above from salts or complexes of the metals cobalt or rhodium. Under the action of synthesis gas, the cobalt or rhodium complexes originally used are converted into the active hydroformylation catalyst.

The concentration of the metal (in the form of the complex) in the organic or aqueous catalyst solution is, based on olefinically unsaturated compound used, from 10^{-6} to 1 mol %, preferably from 10^{-4} to 10^{-1} mol %. Within the ranges indicated, the cobalt concentration required is up to a power of ten higher than the rhodium concentration required.

The reaction of olefinically unsaturated compound with carbon monoxide and hydrogen is carried out at pressures of from about 0.1 to about 300 MPa, preferably from 1 to 15 MPa, with cobalt catalysts requiring higher pressures than rhodium catalysts. The composition of the synthesis gas, i.e. the volume ratio of carbon monoxide and hydrogen, can extend over a wide range and be varied, for example, from 1 : 10 to 10 : 1. In general, use is made of gas mixtures in which the volume ratio of carbon monoxide to hydrogen is about 1 : 1 or deviates only slightly from this value in one or other direction.

The reaction temperature is between about 20 and 180°C, preference being given to from 80 to 150°C. Cobalt catalysts require higher temperatures than catalysts based on rhodium.

The reaction of the reactants present in a liquid or gaseous phase is carried out in conventional reactors. The course of the reaction is decisively influenced by intimate contact between, in the case of the homogeneous systems, a liquid and a gaseous phase, and, in the case of the heterogeneous systems, two liquid phases and a gaseous phase. It is therefore necessary to generate as large as possible a contact surface between the phases. Therefore, synthesis gas and, if desired, also olefin are preferably fed into the liquid phase via distribution devices. In the case of the hydroformylation reaction carried out using a heterogeneous catalyst phase, it is advisable to stir the reaction mixture intensively. If desired, a solubilizer can also be added to the aqueous phase so as to improve the solubility of the olefinic compound in the catalyst. The reaction can be carried out batchwise or, preferably, continuously.

The process of the invention can be successfully applied to the reaction of monoolefins, polyolefins, cyclic olefins and derivatives of these unsaturated compounds. With regard to the molecular size, the olefins used are subject to no restriction; the procedure has been found to be successful for compounds having from 2 to 40 carbon atoms. The olefinically unsaturated compounds can be straight-chain or branched, the double bonds can be terminal or internal. Examples of olefins which can be used in the new process are ethylene, propylene, 1-butene, 2-butene, 1-pentene, 2-methylbut-1-ene, 1-hexene, 2-hexene, 1-heptene, 1-octene, 3-octene, 3-ethylhex-1-ene, 1-decene, 3-undecene, 4,4-dimethylnon-1-ene, dicyclopentadiene, vinylcyclohexene, cyclooctadiene, styrene, 2-vinylnaphthalene. Derivatives of the types of olefins specified which can be hydroformylated using the method claimed are, for example, alcohols, aldehydes, carboxylic acids, esters, nitriles and halogen compounds, allyl alcohol, acrolein, methacrolein, crotonaldehyde, methyl acrylate, ethyl crotonate, diethyl fumarate, diethyl maleate, acrylonitrile. The process is used particularly successfully for the hydroformylation of olefins and olefin derivatives having from 2 to 20 carbon atoms.

If one the carbene ligands in a complex used as catalyst is chiral, i.e. it possesses no symmetry element of the second type according to the Schönflies system, asymmetric inductions occur in the hydroformylation products if the starting materials are prochiral and the metal complex catalyst is used in optically pure form. Chiral products can be prepared in this way.

In the following, the preparation of the new catalysts is first described; the subsequent examples illustrate the invention but do not restrict it to the detailed embodiments.

Example 1: Preparation of chloro(η^4-1,5-cyclooctadiene)(1,3-dimethylimidazolin-2-ylidene)rhodium(I) (catalyst 1)

a) 1,3-Dimethylimidazolin-2-ylidene

8.69 g (38.8 mmol) of 1,3-dimethylimidazolium iodide are dissolved together with 1.03 g (42.7 mmol) of sodium hydride and 0.2 g (1.8 mmol) of potassium tert-butoxide in 50 ml of tetrahydrofuran (THF) and stirred for 4 hours at room temperature in a Schlenk tube having an attached paraffin oil nonreturn valve. The solution is turned yellow by the free carbene formed. The solvent is taken off in a high vacuum and the residue is distilled under vacuum in a microdistillation apparatus. This gives 1,3-

dimethylimidazolin-2-ylidene in the form of a yellow oil. The carbene is immediately dissolved in 60 ml of THF and stored at -30°C.

b) Chloro(η^4-1,5-cyclooctadiene)(1,3-dimethylimidazolin-2-ylidene)rhodium(I)

247 mg (0.5 mmol) of di-(μ-chloro)bis(η^4-1,5-cyclooctadiene)dirhodium are taken up at room temperature in 20 ml of absolute THF and admixed with 192 mg (1 mmol) of 1,3-dimethylimidazolin-2-ylidene. The immediate reaction can be recognized by a color change from pale yellow to deep yellow. The mixture is stirred for a further 15 minutes at room temperature, the solvent is taken off in a high vacuum and the residue is purified by washing with 10 ml of diethyl ether. The product is taken up in 10 ml of methylene chloride and carefully covered with 30 ml of pentane. The resulting yellow crystals are freed of the solvent mixture by decantation and dried in a high vacuum. The compound dissolves very well in chloroform and methylene chloride, dissolves well in THF and toluene, dissolves sparingly in diethyl ether and pentane, giving a yellow color. Even after heating in moist toluene for a number of hours in an oxygen atmosphere, no decomposition takes place. Yield: 310 mg (91 %).

From 5.0 to 20.0 mg (from 0.015 to 0.058 mmol) of this compound are used as catalyst (see table).

<u>Example 2</u>: Preparation of [(η^4-1,5-cyclooctadiene)-bis(1,3-dimethylimidazolin-2-ylidene)rhodium(I)] chloride (catalyst 2)

247 mg (0.5 mmol) of di(μ-chloro)bis(η^4-1,5-cyclooctadiene)dirhodium are taken up at room temperature in 20 ml of absolute THF and admixed with 279 mg (3 mmol) of 1,3-dimethylimidazolin-2-ylidene. The immediate reaction can be recognized by a color change from pale yellow to

deep yellow. The mixture is stirred for a further 3 hours at room temperature, the solvent is taken off in a high vacuum and the residue is purified by washing with 30 ml of diethyl ether. The product is taken up in 10 ml of methylene chloride and carefully covered with 10 ml of pentane. The resulting yellow crystals are freed of the solvent mixture by decantation and dried in a high vacuum. The compound is readily soluble in chloroform and methylene chloride, moderately soluble in THF, water and toluene, insoluble in diethyl ether and pentane. Yield: 410 mg (93 %).

From 5.0 to 20.0 mg (from 0.011 to 0.046 mmol) of this compound are used as catalyst (see table).

Example 3: In situ preparation of catalyst 3

a) 1-Methyl-3-(ethylsulfonic acid sodium salt)imidazolium bromide

205 mg (2.5 mmol) of methylimidazole are stirred without a solvent with 210 mg (1 mmol) of 2-bromoethanesulfonic acid sodium salt for three days at 70°C. After cooling, the residue is washed three times with 30 ml of diethyl ether to remove excess methylimidazole. After drying in a high vacuum (70°C, 10 hours) there remains a white solid which is very readily soluble in water, hardly soluble in organic solvents (such as THF, toluene, pentane). Yield: 280 mg (96 %).

b) Catalyst 3

100 mg of rhodium(III) acetate (0.357 mmol) are dissolved in 25 ml of degassed water and admixed with a solution of 314 mg of 1-methyl-3-(ethyl-2-sulfonic acid sodium salt)imidazolium bromide (1.07 mmol) in 25 ml of degassed water. From 1.0 to 5.0 ml (from 0.00714 to 0.0357 mmol) of this solution (rhodium content 0.0714 mmol per 10 ml of water) are used as catalyst (see table), the active

hydroformylation catalyst forms under hydroformylation conditions.

Example 4: In situ preparation of catalyst 4

a) 1-(Ethyl-2-sulfonic acid sodium salt)-3-(ethyl-2-sulfonate)imidazolium betaine

557 mg (8.2 mmol) of imidazole, dissolved in 20 ml of dimethylacetamide, are admixed with 1.5 ml (10.25 mmol) of triethylamine and 3.45 g (16.3 mmol) of 2-bromoethanesulfonic acid sodium salt. On heating to 120°C, the original suspension becomes clear. After further heating to 160°C, a white precipitate begins to form. To achieve complete reaction, the mixture is heated for 4 hours under reflux. After cooling the solution to room temperature, the white precipitate is filtered off and washed twice with 20 ml of ethanol and ether each time.

b) Catalyst 4

100 mg of rhodium(III) acetate (0.357 mmol) are dissolved in 25 ml of degassed water and admixed with a solution of 328 mg (1.07 mmol) of 1-(ethyl-2-sulfonic acid sodium salt)-3-(ethyl-2-sulfonate)imidazolium betaine in 25 ml of degassed water. From 1.0 to 5.0 ml (from 0.00714 to 0.0357 mmol) of this solution (rhodium content 0.0714 mmol per 10 ml of water) are used as catalyst (see table), the active hydroformylation catalyst forms under hydroformylation conditions.

Example 5: In situ preparation of catalyst 5

a) 1-Methyl-3-(butyl-4-sulfonate)imidazolium betaine

Methylimidazole (8.21 mg, 10 mmol) is stirred without solvent with 1,4-butanesultone (1361 mg, 10 mmol) at room temperature for 3 days. After solidification of the mass, it is washed 3 times with toluene and dried in a high vacuum. The white solid is readily soluble in water, less readily soluble in organic solvents. Yield: 2100 mg (96 %).

b) Catalyst 5

100 mg of rhodium(III) acetate (0.357 mmol) are dissolved in 25 ml of degassed water and admixed with a solution of 234 mg (1.07 mmol) of 1-methyl-3-(butyl-4-sulfonate)-imidazolium betaine in 35 ml of degassed water. From 1.0 to 5.0 ml (0.02975 to 0.00595 mmol) of this solution (rhodium content 0.0595 mmol per 10 ml of water) are used as catalyst (see table), the active hydroformylation catalyst forms under hydroformylation conditions.

<u>Example 6</u>: In situ preparation of catalyst 6

10.0 mg of rhodium(III) hexanoate (0.0223 mmol) and 14.6 mg of 1,3-dimethylimidazolium iodide (0.0669 mmol) are weighed into the glass insert of an autoclave and admixed with 25 ml of toluene. This suspension is used directly as catalyst (see table), the active hydroformylation catalyst is formed under hydroformylation conditions.

<u>Example 7</u>: Hydroformylation of olefins

From 1000 to 100 000 equivalents of an olefin are reacted with synthesis gas while stirring (about 150 min^{-1}) in a 250 ml stirred autoclave (Roth Laboratory Autoclave model H 10781 with glass insert) in the presence of from 5 to 20 mg of the catalysts prepared according to the Examples 1 and 2 and dissolved in toluene or from 1.0 to 5.0 ml of the aqueous catalyst solutions prepared according to the Examples 3 to 5. The synthesis gas contains H_2 and CO in a volume ratio of 1 : 1, the total pressure is 10 MPa, the propene partial pressure (when using propene as olefin) is 1.2 MPa. As soon as the pressure drops to from about 3.0 to 4.0 MPa during the course of the reaction, further synthesis gas is injected.

After cooling to room temperature, the product is analyzed by means of gas chromatography/mass spectrometry and/or purified by distillation and characterized.

Notes to the table

* Exclusively 3,4-dimethylpentanal could be identified as product by means of gas chromatography/mass spectrometry.

** n-Heptenal (33.8 %) and 2-methylhexanal (66.2 %) could be identified as products by gas chromatography/mass spectrometry.

<u>Table</u> - Hydroformylation of olefins

No.	Catalyst	Olefin	Cat./ olefin	Solvent	n/iso ratio	Conversion (%)	Observations
1	1	Propene	1:100,000	Toluene	1.0:1.0	>99(60h)	
2	1	1-Hexene	1:100,000	Toluene	1.0:1.0	85(60h)	
3	1	Styrene	1:2000	Toluene	1.16:1.0	100(20h)	
4	1	Tetramethylethylene	1:1000	Toluene	*	82(20h)	Isomerization of starting material
5	1	2-Hexene	1:2500	Toluene	**	95(20h)	Isomerization of starting material
6	2	1-Hexene	1:2500	Toluene	2.0:1.0	85(20h)	Catalyst sparingly soluble in toluene
7	2	Propene	1:10000	Water	1.2:1	85(20h)	Catalyst soluble in butyraldehyde phase after catalysis
8	3	Propene	1:10,000	Water	2.1:1	85(20h)	Catalyst also soluble in aqueous phase after catalysis; red
9	4	Propene	1:10,000	Water	1.9:1	92(20h)	Catalyst also dissolved in aqueous phase after catalysis; red
10	5	Propene	1:10,000	Water	1.4:1	65(20h)	Catalyst also dissolved in aqueous phase after catalysis; red
11	6	Propene	1:10,000	Toluene	1.4:1	70(20h)	

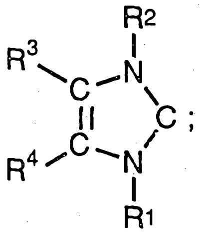
While only a limited number of specific embodiments of the present invention have been expressly disclosed, it is, nonetheless, to be broadly construed and not to be limited except by the character of the claims appended hereto.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

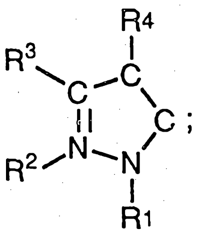
1. A process for preparing aldehydes by reaction of a compound selected from the group consisting of monoolefins, polyolefins, cycloolefins, or derivatives thereof with carbon monoxide and hydrogen at temperatures of from 20° to 180° C. and pressures of from 0.1 to 30 MPa in the presence of complexes of cobalt or of rhodium as a catalyst, wherein said complexes are of the formula

$$[L_aM_bX_c]^n(A)_n, \qquad (I)$$

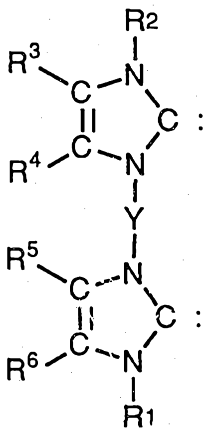
wherein M is cobalt or rhodium as a central atom, X's are individually monodentate or multidentate, charged or uncharged ligands bound to said central atom and L's are individually ligands bound to said central atom and are selected from the group consisting of monocarbenes and dicarbenes of the formulas



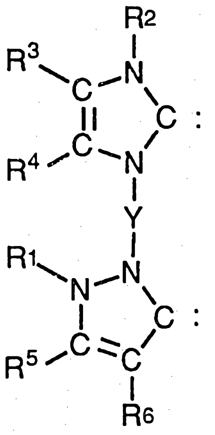
(II)



(III)



(IV)



(V)

wherein R^1, R^2, R^3, R^4, R^5, and R^6 are individually selected from the group consisting of straight or branched chain, sulfonated or unsulfonated alkyls having 1 to 7 carbon atoms; sulfonated or unsulfonated aliphatic monocyclics and polycyclics having 5 to 18 carbon atoms; sulfonated or unsulfonated alkenyls having 2 to 5 carbon atoms; sulfonated or unsulfonated aryls having 6 to 14 carbon atoms; and sulfonated or unsulfonated aralkyls having 7 to 19 carbon atoms; R^1 and R^2 are also selected from the group consisting of —$(CH_2)_mPR_2$, wherein m=1, 2, 3 or 4 and R=benzyl, phenyl, substituted phenyl, naphthyl; —$(CH_2)_mNR'_2$ (wherein R'=alkyl, vinyl, allyl, benzyl, and aryl); and —$(CH_2)_mOR''$ (wherein R"=alkyl); R^3, R^4 R^5 and R^6 can also be hydrogen; R^3 together with R^4, and R^5 together with R^6, may individually form fused and sulfonated or unsulfonated radicals having 3 to 7 carbon atoms, R^1, R^2, R^4, or R^6, together with X may form a ring, Y is selected from the group consisting of saturated or unsaturated, straight or branched chain alkylidenes having 1 to 4 carbon atoms, dialkylsilylenes, and tetraalkyldisilylenes; A is a singly charged anion or the chemical equivalent of a multiply charged anion, b is an integer from 1 to 3, a is an integer from 1 to 4 times b, and c=0 or an integer from 1 to 4 times b, and n' =0 or an integer from 1 to 6.

2. The process of claim 1 wherein R" is selected from the group consisting of methyl, vinyl, allyl, benzyl, and phenyl.

3. The process of claim 1 wherein the X's are selected from the group consisting of hydrogen, hydrogen ion, halogens, halide ions, pseudohalides, carboxylate ions, sulfonate ions, alkyls having 1 to 7 carbon atoms, amides, alkoxides, acetylacetonates, carbon monoxide, nitrogen monoxide, nitriles, isonitriles, monoolefins, diolefins, alkynes, and π-aromatic radicals.

4. The process of claim 1 wherein R^1, R^2, R^3, R^4, R^5, and R^6 are individually methyl, isopropyl, tert-butyl, benzyl, triphenylmethyl, phenyl, tolyl, xylyl, or mesityl.

5. The process of claim 1 wherein R^3 and R^4 are individually hydrogen or methyl.

6. The process of claim 1 wherein R^3 together with R^4, R^5 together with R^6, are individually $(CH)_4$, $(CH_2)_4$, or $(CH_2)_5$.

7. The process of claim 1 wherein Y is methylene, dimethylmethylene, diphenylmethylene, 1,3-phenylene, or ethylidene.

8. The process of claim 1 wherein Y is dimethylsilylene or tetramethyldisilylene.

9. The process of claim 1 wherein a is 1 or 2.

10. The process of claim 1 wherein b is 1.

11. The process of claim 1 wherein n is 0 to 3.

12. The process of claim 1 wherein A is halide, pseudohalide ion, tetraphenylborate ion, tetrafluoroborate ion, hexafluorophosphate ion, acetate ion, tetracarbonylcobaltate ion, hexafluoroferrate ion, tetrachloroferrate ion, tetrachloroaluminate ion, or tetrachloropalladate ion.

13. The process of claim 1 wherein said reaction is carried out in the presence of a catalyst homogeneously dissolved in a reaction medium.

14. The process of claim 1 wherein said reaction is carried out in the presence of an aqueous catalyst solution.

15. The process of claim 1 wherein a concentration of said central atom is an organic phase or in an aqueous phase is 10^{-6} to 1 mol %, based on said compound.

16. The process of claim 15 wherein said concentration is 10^{-4} to 10^{-1} mol %.

17. The process of claim 1 wherein said reaction is carried out at 80° to 150° C.

18. The process of claim 1 wherein said compound has 2 to 40 carbon atoms.

DATED this 16th day of February, 1998.
HOECHST AKTIENGESELLSCHAFT

WATERMARK PATENT & TRADEMARK ATTORNEYS
290 BURWOOD ROAD
HAWTHORN VICTORIA 3122
AUSTRALIA

KJS:JPF:JL VAX doc 20 AU4070595.WPC

Frankfurt, December 23, 1994
FPR/rcht-sei Hoe94/Y010

Hoechst Aktiengesellschaft, 65926 Frankfurt am Main

Abstract

The invention relates to the hydroformylation of olefins and olefinically unsaturated compounds in the presence of cobalt or rhodium complexes which contain as complexing ligands heterocyclic carbenes and in addition, if desired, further ligands.