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Application of transition metals in hydroformylation: annual survey covering the year 1996

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Contents

Abstract

Hydroformylation in homogeneous and heterogeneous systems, and hydroformylation related reactions of carbon monoxide are reviewed.

Keywords: Hydroformylation; Water-gas shift reaction; Reduction of carbon monoxide; Reduction of carbon dioxide; Transition metals

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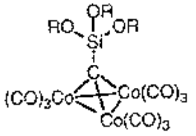
1. Hydroformylation

1.1. Homogeneous systems

1.1.1. Cobalt catalysts

The catalytic activity of $Co_2(CO)_6(L)_2$ complexes ($L = P(CH_2CH_2CN)_3$, $P(CH_2CH_2CO_2CH_3)_3$, $P(CH_2CH_2CH_2OCH_3)_3$ and $P(CH_2CH_2CH_2OCH_2CH_3)_3$) in hydroformylation of 1-hexene and propene was tested. The influence of solvent, reaction temperature, carbon monoxide partial pressure, and excess of free phosphine in solution on the chemo- and regioselectivity of the reaction was investigated and the results were compared with those obtained when using $Co_2(CO)_8$ or $Co_2(CO)_6(PBu_3)_2$ as the catalyst precursors [1].

Hydroformylation of 1-octene in the presence of a heteronuclear Co_2Ni complex and of alkylidenecarbonyl cobalt clusters $Co_3(CO)_9(\mu_3\text{-CR})$ (R = H, Me, Ph, CO_2Me, CO_2Et, CO_2^iPr, CO_2^tBu, Cl, Br, OMe) and their triphenylphosphine derivatives has been studied. The nature of the catalytically active sites and their formation and transformation during the reaction have been established by infrared spectroscopy [2]. The catalytic activity of the tricobalt cluster complex 1 in hydroformylation of 1-hexene was examined at 120 C and 80 bar $CO{:}H_2 = 1{:}1$ in toluene (R = H) and in polyethylene glycol ($R = CH_2CH_2(OCH_2CH_2)_9OH$) as the solvent.



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High conversion (up to 99.9%) and high aldehyde selectivity (up to 95%) was achieved. In the latter case the hydroformylation is performed under two-phase conditions. The addition of phosphanes was found to improve the regioselectivity [3]. Group 13 heterosiloxanes $[Co_3(CO)_9CSiO_3E \cdot THF]_4$ (E = Al, Ga, In) were tested as catalysts in 1-hexene hydroformylation at 120 C and 70 bar $CO{:}H_2 = 1{:}1$. The Al- and Ga-containing heterosiloxanes show a better hydroformylation activity compared to the In analog [4].

The Shell hydroformylation process for the production of aliphatic alcohols used in detergent production was described [5].

The mechanism of olefin hydroformylation in the presence of a cobalt carbonyl–pyridine complex as a catalyst precursor was studied using infrared spectroscopy [6]. The kinetics of hydroformylation of propylene tetramers in the presence of the catalyst precursors $Co_2(CO)_8$, $Co_2(CO)_8$/trilaurilphosphine, and a pyridine cobalt carbonyl complex were studied. A good agreement between the model proposed and experimental data was shown [7].

The importance of the macromolecule–metal complex interactions and the design of appropriate catalyst systems was illustrated among others for the hydroformylation/hydroxymethylation of a number of polymers [8].

A theoretical study based on density functional theory was carried out on the reaction pathways leading to acetaldehyde and ethanol formation from the hydrogenation of the coordinatively unsaturated acetylcobalt tricarbonyl complex. It was found that, in the H_2-induced acetaldehyde elimination reaction, the energy barrier for the oxidative addition/reductive elimination process is only 36.3 kJ mol^{-1}. The production of ethanol from hydrogenation of acetaldehyde through a hydroxymethyl intermediate has an energy barrier of 42.3 kJ mol^{-1}. It was concluded that the catalytic generation of alcohols does not proceed via the formation of a hydroxycarbene intermediate but rather through further hydrogenation of the aldehyde molecules [9].

1.1.2. *Rhodium catalysts*

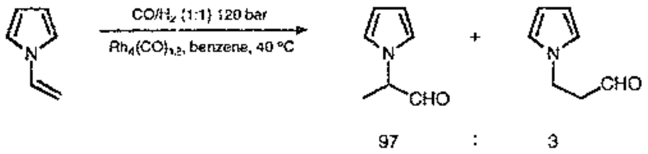
^{2}H NMR investigation of the products of the rhodium-catalyzed deuteroformylation of 1,1-diphenylethene obtained at partial substrate conversion (15 and 34%) at 100 °C and 100 bar $CO:D_2 = 1:1$ has shown the formation of monodeuterated olefin 1,1-diphenylethene-2-d_1 and the labeled normal aldehyde arising from this substrate in addition to the expected diphenylpropanal-1,3-d_2. These results demonstrate that a tertiary alkyl-rhodium intermediate is formed, under hydroformylation conditions, in a larger amount than the normal isomer, but it undergoes β-hydride elimination only, without formation of the branched aldehyde [10].

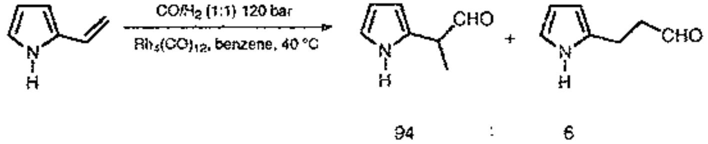
High α-regioselectivity was found in the rhodium-catalyzed hydroformylation of vinylpyrroles leading mainly to the branched aldehyde isomer in moderate to good yield [11].

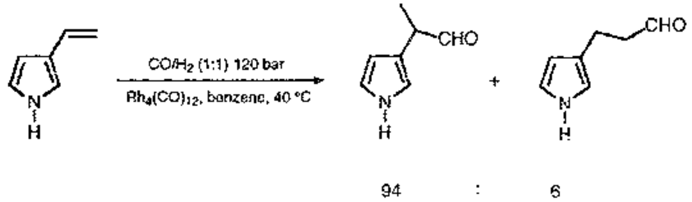
The influence of alkyl substituents in 1-alkene substrates in the rhodium-catalyzed hydroformylation in the presence of tris(2-*tert*-butyl-4-methylphenyl) phosphite was studied and compared with that observed for the reaction involving the triphenylphosphine-modified catalyst. Under mild conditions (70 °C, 20 bar $CO:H_2 = 1:1$) the rates are only slightly affected by the alkyl substituents. The selectivity towards the linear aldehyde increases progressively with substitution, from 66% for 1-octene up to 100% for 3,3-dimethyl-1-butene [12].

Hydroformylation of 1-octene and styrene was studied using $[Rh(CO)_2acac]$ with bulky diphosphite ligands such as **2** or **3** as catalyst precursor. For styrene the product selectivity was found to depend strongly on the reaction temperature. Thus, a branched to normal ratio of 19 was found for ligand **2** at 40 °C versus a branched to normal ratio of 0.19 for ligand **3** ($R = {}^{t}Bu$, $R' = H$) at 120 °C. A bulky and bisequatorially coordinating diphosphite is required to obtain a high regioselectivity for linear aldehydes, while flexible diphosphites or equatorially-axially coordinating diphosphites lead to an enhancement of the branched aldehydes [13].

A new catalytic system for one-step oxosynthesis of octanol from 1-heptene was described. $Rh_2(OAc)_4$ and $[Rh(NH_3)_5Cl]Cl_2$ with a tertiary phosphine were found to be effective catalyst precursors for 1-heptene hydroformylation to give octanol. The effect of various parameters on the reaction was studied and optimum values were determined. When an autoclave is charged at 120 °C for 24 h with 1-heptene


N
CO/H2 (1:1) 120 bar
Rh4(CO)12, benzene, 40 °C
N
CHO
+
N
CHO
97
:
3


N
H
CO/H2 (1:1) 120 bar
Rh4(CO)12, benzene, 40 °C
CHO
N
H
+
N
H
CHO
94
:
6


N
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CO/H2 (1:1) 120 bar
Rh4(CO)12, benzene, 40 °C
CHO
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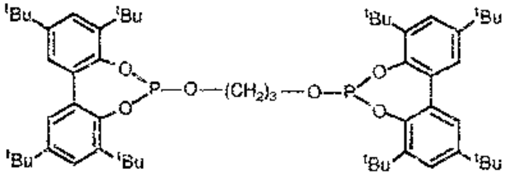
tBu
tBu
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P
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(CH2)3
O
P
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O
tBu
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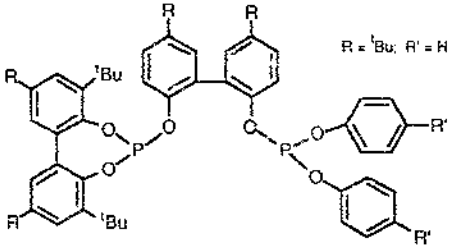
tBu

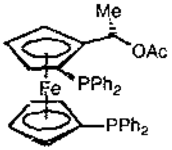
2


R
R
R = tBu; R' = H
R
tBu
O
P
O
O
O
P
O
O
R'
R'
R
tBu

3

(2 mL), $Rh_2(OAc)_4$ (11 mg), ethanol (8 mL) and tributylphosphine (P:Rh molar ratio = 4:1) under syngas pressure of 50 bar (H_2:CO = 2:1), it gives an alcohol yield of above 95% with *n*-octanol/*iso*octanol ratio up to 2.0:1 [14].

Styrene hydroformylation was found to be catalyzed by $Rh(acac)(CO)_2$ in the presence of 4 equiv. of the ligands **4**–**6** at 80 °C and 6 bar of syngas to yield both normal and branched aldehydes. The regioselectivity of the hydroformylation is: branched/normal ≈2 for ligand **4**, and a branched/normal ≈4 for ligand **5** and **6** [15].



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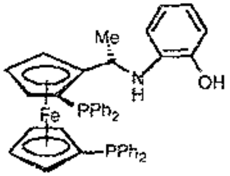

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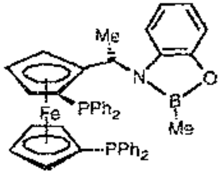

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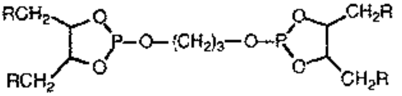
Rhodium carbonyl $[Rh_6(CO)_{16}]$ and tricyclohexylphosphine, in the presence of CO and HCOOH, was found to be an efficient catalytic system for the regioselective conversion of alkenes containing a variety of functional groups, into branched and linear aldehydes at 50 °C in 1,2-dimethoxyethane solution [16].

The kinetics of hydroformylation of styrene were studied using the rhodium-complex $Rh(CO)Cl(TPP)_2$ (TPP = 1,2,5-triphenyl-1H-phosphole (**7**)) as a catalyst precursor. The rate of hydroformylation was found to be first order in styrene, $Rh(CO)Cl(TPP)_2$ and partial pressure of dihydrogen, and negative first order in partial pressure of carbon monoxide. The reaction orders are consistent with a mechanism including dissociation of carbon monoxide from $Rh(CO)Cl(TPP)_2$ complex formed outside the catalytic cycle during an induction period, leading to a 14-electron acylrhodium intermediate $RCORh(TPP)_2$ and the rate determining hydrogenolysis of the latter complex [17].

7

The rhodium–phosphine complex catalyst $Rh(CO)(acac)PPh_3$ for 1-hexene hydroformylation was studied at 10 bar $CO/H_2 = 1$ and 25–120 °C by in situ ^{1}H-NMR spectroscopy. The formation of a rhodium hydride complex was observed at room temperature from the precursor rhodium complex. This intermediate complex began to decompose at 100 °C and disappeared completely at 120 °C. The observed hydroformylation activity was proportional with the hydride signal of the intermediate complex [18].

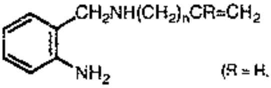
Novel, chiral, aza-15-crown-5-containing phosphite ligands such as **8** were synthesized and characterized and used as ligands in rhodium-catalyzed hydroformylation of alkenamides and styrene [19].



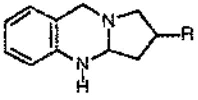
(RH = aza-15-crown-5)

8

Rhodium-catalyzed hydroformylation of **9** with H_2/CO was found to give hexahydropyrrolo- and hexahydropyrido-[2,1-*b*]quinazolines, e.g. **10**. Reactions of N-allyl derivatives give a single regioisomer, and reactions of but-3-enyl analogs give mixtures of pyrrolo and pyrido derivatives [20].



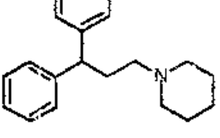
(R = H, Me; n = 1, 2)

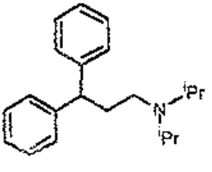


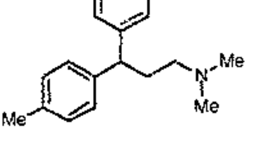
9 **10**

Hydroformylation of unsaturated alcohols catalyzed by $\mathrm{Rh(CO)_2(acac)}$ modified with different phosphorus ligands was studied. The hydroformylation of 3-buten-2-ol, 1-octen-3-ol and 5-hexen-1-ol at 60 and 80 °C under 10 bar of $H_2/CO = 1$ give as main products 2-hydroxy-methyltetrahydrofuran, 2-hydroxy-5-pentyltetrahydrofuran and hydroxy aldehydes (7-hydroxyheptanal + 2-methyl-6-hydroxyhexanal), respectively. The highest catalytic activity was found in systems modified with $\mathrm{Ph_2P(CH_2)_4PPh_2}$ and $\mathrm{P(O\text{-}}m\mathrm{\text{-}MeC_6H_4)_3}$ [21].

A novel efficient synthesis of three important pharmaceuticals: Fenpiprane (**11**), Diisopromine (**12**) and Tolpropamine (**13**), starting from simple 1,1-diarylethenes has been described. The substrates undergo rhodium-catalyzed hydroformylation with high selectivity to 3,3-diarylpropanals which were easily transformed to the corresponding tertiary amines by platinum-catalyzed reductive amination according to literature procedures in 80–85% yield [22].





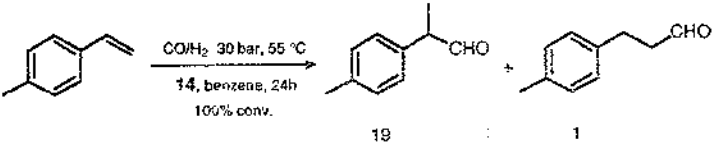


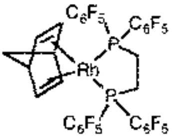
11 **12** **13**

Poly(4-vinylpyridine)rhodium complex catalysts were used as catalysts for olefin hydroformylation [23]. Investigations by in situ FT-IR, ^{1}H- and ^{1}H{^{31}P}-NMR spectroscopy have shown that an unusual two-nucleus rhodium(II) complex *rac*-$\mathrm{[Rh_2H_2(\mu\text{-}CO)_2(CO)_2(et,ph\text{-}P4)][BF_4]_2}$ (et,ph-P4 = $\mathrm{Et_2PCH_2CH_2P(Ph)CH_2P(Ph)}$

$-CH_2CH_2PEt_2$) is the catalytically active species in alkene hydroformylation using *rac*-[Rh_2(NBD)$_2$(et,ph-P4)][BF_4]$_2$ as catalyst precursor [24,25].

A rhodium diphosphine catalyst **14** containing electron withdrawing substituents on the ligand was found to be highly regioselective in the hydroformylation of vinylarenes giving high branched/linear product ratios [26].





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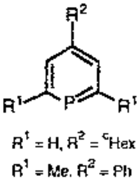
Highly regioselective rhodium-catalyzed hydroformylation under mild conditions with new classes of π-acceptor ligands **15–22** has been reported. For example: using 0.357M Rh(CO)$_2$(acac) and **21** in 1:2 molar ratio in toluene at 20 °C and 50 bar CO/H_2 = 1, 98% conversion of styrene in 22 h resulted in 24.8:1 = branched:linear aldehydes [27].

Factors controlling the selectivity for aldehyde formation in a new rhodium–phosphine oxide $R_2N(CH_2)_nP(O)R'_2$ (R' = Ph, cyclohexyl; n = 0,1,2,3; R = Me, Et, Me_2CH or R_2N = pyridyl) system has been investigated. It was found that: ligands having bulkier amino groups decrease the yield of the aldehyde slightly, ligands having amino groups with low basicity decrease the rate of the hydroformylation dramatically, the electronic properties of the phosphine oxide group have no influence on the hydroformylation reaction, and uncoordinating solvents of low polarity such as dichloromethane, chloroform and toluene, gave the best reaction rate and selectivity. Spectroscopic investigation of the hydroformylation of styrene catalyzed by rhodium with ligand $Rh_2P(O)CH_2NMe_2$ has shown that the ligand is coordinated by the amino and the phosphine oxide groups under 1 bar CO–H_2 and only by the amino group under 40 bar CO–H_2 [28].

The rhodium-catalyzed hydroformylation of higher alkenes was studied using novel amphiphilic diphosphines **22–26**. With 1-octene at 80 °C and 20 bar CO:H_2 = 1 in toluene, high normal:branched ratios (up to 51:1) were found with 6–8% of isomerized octenes. The rate of hydroformylation using **23–26** was found to be first order and approximately first order, respectively, in rhodium and 1-octene concentration. The order in carbon monoxide pressure is negative and that in dihydrogen pressure slightly negative. The recovery of the catalyst was also studied [29].



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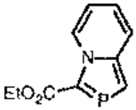

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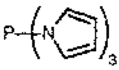

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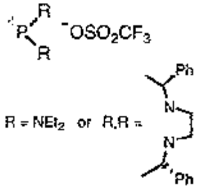

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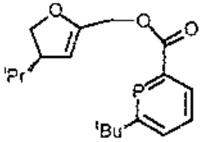

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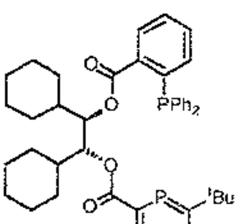

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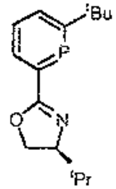

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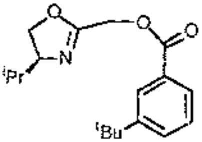

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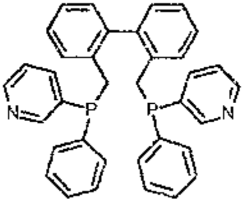

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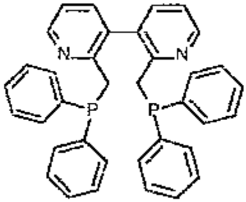

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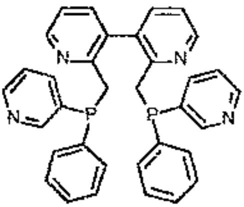

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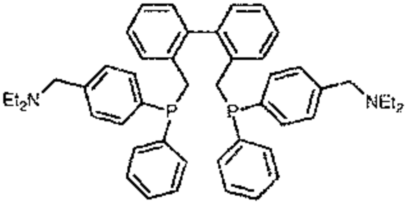

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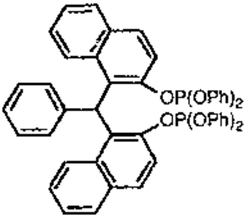
Rhodium complexes with the phosphite ligands **27** and **28** were found to catalyze the hydroformylation of cyclohexene with average turnover frequencies of 428 and 344 mol/mol h, respectively, over 4 h at 60 °C and 20 bar CO–H_2 [30].



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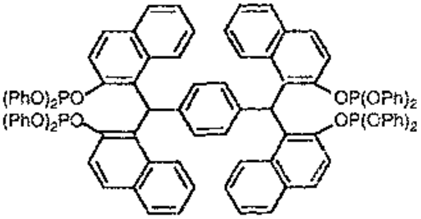

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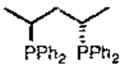
Effects of concentration and aryl conjugation on regioselectivity of hydroformylation of 1-dodecene and terminal olefins containing an aromatic substituent in the presence of rhodium(I) bis(triphenylphosphite)acetylacetonate were studied [31]. The applicability of acetylcellulose, polysulfonamide, polyamide and tetrafluoroethylene–vinylidene fluoride copolymer based membranes was studied in separation of homogeneous rhodium hydroformylation catalysts. It was found that rhodium complexes with phosphinated polybutadiene can be separated using polysulfonamide membranes. The catalytic properties of the rhodium complexes do not change after six operation cycles [32]. The stability of rhodium carbonyl catalysts modified by triphenylphosphine was studied under hydroformylation conditions and the role of rhodium phosphidocarbonyl clusters in deactivation of the catalyst was examined [33].

Technology and apparatus for hydroformylation of C_4–C_6 olefins in the presence of a modified rhodium carbonyl catalyst has been described. The negative influence of acetylene, dienes, carbon dioxide, oxygen and iron pentacarbonyl has been observed [34]. Oxidative regeneration of triphenylphosphine-modified rhodium catalysts for olefin hydroformylation by air was studied [35]. A catalyst obtained from (acetylacetonato)dicarbonylrhodium and tris(*p*-nonylphenyl)phosphite was studied in the hydroformylation of 1-hexene by IR and NMR spectroscopy. It was found that the catalyst is deactivated by hydrolysis and oxidation of the phosphite ligand [36]. Carbonyl–rhodium complexes formed during formaldehyde hydroformylation under synthesis-gas pressure in *N*,*N*-dimethylacetamide were investigated by infrared spectroscopy [37]. Hydroformylation with extremely low levels of rhodium has been applied for the highly selective, high turnover process for the production of *iso*valeraldehyde [38].

Asymmetric hydroformylation of styrene using [Rh(μ-OMe)(COD)] complex with (+)-BDPP (**29**) as the chiral auxiliary ligand was studied. The enantiomeric excess of (*S*)-2-phenyl-propanal observed heavily depends on the excess of diphosphine used and enantiomeric excesses up to 60% are achieved [39].

Asymmetric hydroformylation of conjugated dienes such as 1-vinylcyclohexene.



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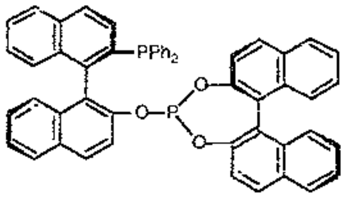
(*E*)-1-phenylbuta-1,3-diene and 4-methylpenta-1,3-diene using (*R,S*)-BINAPHOS-rhodium(I) complexes ((*R,S*)-BINAPHOS = **30**) as catalysts was found to give optically active β,γ-unsaturated aldehydes in high regio- (81–91%) and enantioselectivities (84–97% ee) [40].



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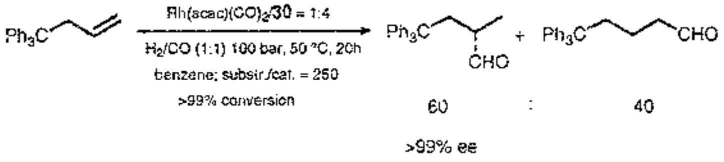
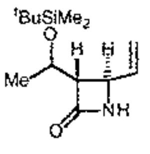
Asymmetric hydroformylation catalyzed by a rhodium(I)-(*R,S*)-BINAPHOS complex has been studied with respect to the substituent effects in olefins on the regioselectivity. Olefins bearing the larger substituents at the allylic position were found to give higher *iso*/normal selectivity. Results of deuteroformylation of 4,4,4-triphenyl-1-butene suggested that the higher *iso*/normal ratio may be attributed to the accelerated carbon monoxide insertion of the corresponding *iso*-alkylrhodium intermediate [41].



Asymmetric hydroformylation of **31** using a rhodium(I) complex of a new chiral phosphine-phosphinite **32** as catalyst precursor, afforded **33** along with its epimer and normal-isomer in 95% total yield at 60°C and 50 bar CO/H$_2$ = 1 [42].



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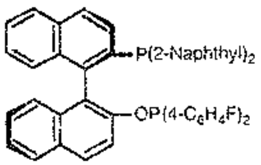

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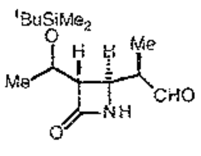
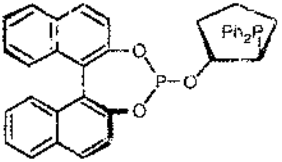


33

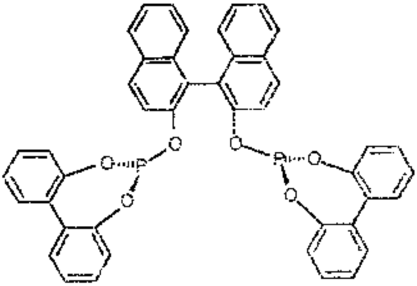
Asymmetric hydroformylation of vinyl sulfides $RSCH=CH_2$ (R = Et, $CHMe_2$, CMe_3, cyclohexyl, Ph, 4-MeC_6H_4)], allyl sulfides $RSCH_2CH=CH_2$ (R = CMe_3, Ph) and allyl sulfone $PhSO_2CH_2CH=CH_2$ catalyzed by (*R,S*)-BINAPHOS/Rh(acac)$(CO)_2$ afforded the corresponding branched aldehydes RSCH(CHO)Me, $RSCH_2CH(CHO)Me$ and $RSO_2CH_2CH(CHO)Me$, respectively, as major products in 60–89% ee. Using bulkier substituents on the sulfur in vinyl sulfides gave the branched aldehydes in higher regio- and enantioselectivities [43].

Chiral phosphinephosphites having axial and central chirality have been tested in hydroformylation. For example, allyl acetate undergoes hydroformylation in the presence of Rh(acac)$(CO)_2$ and **34** (1:5 ratio) to give a 64:36 ratio of $AcOCH_2CH(CHO)Me$ and $AcO(CH_2)_3CHO$ with 44% ee [44].



34

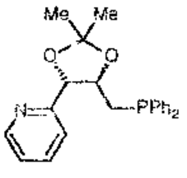
A novel bis(phosphite) rhodium complex, $Rh_4(\mu\text{-bpnap})(CO)_{10}$ (bpnap = **35**), was found to be an effective catalyst precursor for the isomerization and hydroformylation of 1-octene, giving, for the latter reaction, moderate linear branched selectivity for the product aldehydes. The hydroformylation of α-methylstyrene with Rh(acac)$(CO)_2$ and **35** gives essentially no enantiomeric excess of 3-phenylbutanal [45].



35

Homochiral derivatives of 2,2-dimethyl-1,3-dioxolane, **36–38**, were prepared from L-(+)-tartrate and assessed among others in rhodium- and platinum-catalyzed hydroformylation and palladium-catalyzed hydrocarbethoxylation of styrene. Generally low enantioselectivity was found [46].

Hydroformylation of various methallyl-*ortho*-diphenylphosphino benzoates **39**



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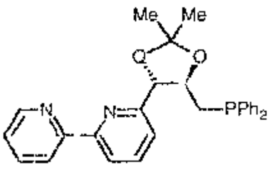

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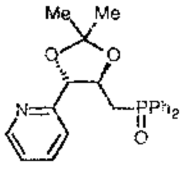

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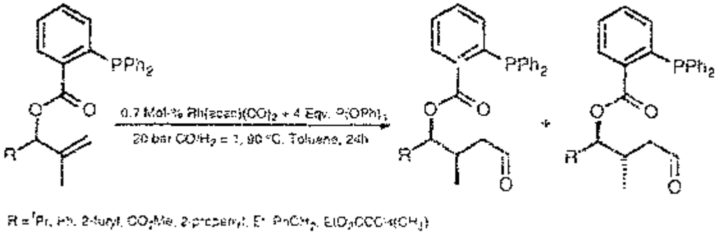
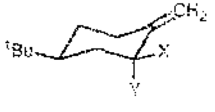
using a Rh(acac)(CO)$_2$/P(OPh)$_3$ catalyst system resulted in the corresponding *syn*-aldehyde **40** as main isomer in good to excellent yields and diastereoselectivities [47].



39 syn-**40** anti-**40**

The diastereoselective hydroformylation of **41** and **42** resulted in threo- and erythro-γ-hydroxyalkanal derivatives in ratios up to 82:18, using 1 mol% Rh(acac)(CO)$_2$ as catalyst precursor at 80 °C and 80 bar CO/H$_2$ = 1 [48].

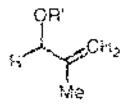
See also Refs. [50,52,64,66,71,92].



X = OR, Y = H, R = H, pivaloyl

X = H, Y = OR, R = H, pivaloyl

41



R = octyl, cyclohexyl

R' = H, COPh, pivaloyl, Me$_3$CPh$_2$Si, Me$_3$CMe$_2$Si, COMe

42

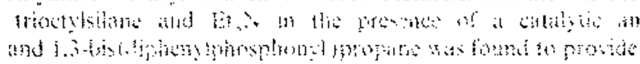
1.1.3. *Other metals as catalysts and bimetallic catalysts*

Ru$_3$(CO)$_{12}$/1,10-phenanthroline-catalyzed hydroformylation of propene and 1-octene under 80 bar of CO/H$_2$ = 1 at 120–130 °C in an amide solvent gives the corresponding aldehydes in 65–93% and 49–55% yield, respectively, and with high linearity (*n*-selectivity ≥95%) [49].

(1*S*,5*S*)-(−)- and (1*R*,5*R*)-(+)-β-pinene were hydroformylated in toluene to give (1*S*,2*R*,5*S*)- and (1*R*,2*S*,5*R*-10)-formylpinane with up to 95% diastereoselectivity using bimetallic $CoRh(CO)_7$ as a catalyst. At 70–125°C and under 60 bar of syngas, the yields of hydroformylated products do not exceed 30% because of the concomitant isomerization of β- to α-pinene. The catalyst was recovered as soluble cobalt carbonyl derivatives and a crystalline precipitate that contains most of the rhodium, mainly as hexarhodium hexadecacarbonyl. Comparable yields and diastereoselectivities were obtained from reactions in THF with a mixture of tetrarhodium dodecacarbonyl and $[N(PPh_3)_2]Cl$ as the catalyst precursor. The corresponding (1*S*,2*R*,5*S*)- and (1*R*,2*S*,5*R*-10)-formylpinanes, along with the corresponding alcohols were obtained diastereoselectively by use of bimetallic cobalt–rhodium or homometallic rhodium carbonyl catalysts modified with bis(diphenylphosphino)ethane [50].

The catalytic activity of new bimetallic rhodium–zirconium catalysts composed with $Rh(acac)(CO)_2$ and $Cp_2Zr(CH_2PPh_2)_2$ or $Cp_2ZrH(CH_2PPh_2)$ in 1-hexene, 1,5-hexadiene and 1,7-octadiene hydroformylation was studied at 80°C, 10 bar $CO/H_2 = 1$ [51]. The catalytic activity of bimetallic systems containing the rhodium complex $HRh\{P(OPh)_3\}_4$ or $HRh(CO)\{P(OPh)_3\}_3$ and the zirconium(IV) complex $Cp_2ZrH(CH_2Ph)$ was tested in the hydroformylation reaction of 1-hexene and *E*-, *Z*-2-hexene at 80°C and 10 bar $CO/H_2 = 1$. An increase in *n*/*iso* ratio from 2.2 to 3.5 and from 0.4 to 3.7 was observed, respectively, in 1-hexene hydroformylation in comparison with the rhodium only systems. The selectivity increase is caused by the inhibiting effect of the bimetallic Rh–Zr catalyst on 1-hexene to *E*-, *Z*-2-hexene isomerization and *E*-, *Z*-2-hexene hydroformylation [52].

2-Aminostyrenes were found to react with carbon monoxide and dihydrogen in the presence of catalytic quantities of palladium acetate and tricyclohexylphosphine at 100°C and 40 bar $CO/H_2 = 5$ to afford five-membered ring lactams in high yield and selectivity, e.g.



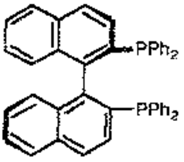
95% yield

2-Allylphenols as reactants in the above reaction gave five- or seven-membered ring lactones [53].

Hydroformylation of aryl and enol trifluoromethanesulfonates in the reaction with CO, trioctylsilane and Et_3N in the presence of a catalytic amount of $Pd(OAc)_2$ and 1,3-bis(diphenylphosphino)propane was found to provide a variety of aromatic and α,β-unsaturated aldehydes [54].

Asymmetric hydroformylation of styrene with $[Pt((S,S)-BDPP)_2]^{2+}(SnCl_3^-)_2$ as catalyst precursor gave chemo-, regio- and enantio-selectivities different from those obtained with the covalent $PtCl(SnCl_3)[(S,S)\text{-}BDPP]$ as catalyst precursor [55]. Asymmetric hydroformylation of styrene catalyzed by platinum(II) alkyl complexes, $[Pt(CH_3)Cl(P\text{–}P)]$, containing atropisomeric diphosphines, P–P = **43–45**, in the presence of $SnCl_2$ has been studied.

At 50°C and 100 bar $CO/H_2 = 1$ the branched aldehyde was obtained with moderate regioselectivity. Good enantioselectivities (up to 75%) were obtained using **44** as



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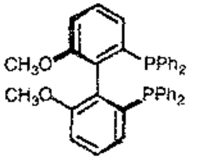

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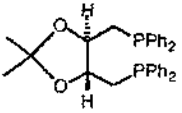


45

the diphosphine ligand. The chirality of 2-phenylpropanal obtained in toluene or in tetrahydrofuran was found to be the opposite to that produced in dichloromethane or acetone. An unusual increase of the rate and enantioselectivity of the reaction with increasing partial pressure of carbon monoxide was observed using the diphosphine **43** [56].

See also Refs. [2,46,57,61].

1.2. *Heterogeneous systems*

1.2.1. *Supported complexes*

The hydroformylation of 1-heptene catalyzed by homogeneous and heterogeneous $Ru_3(CO)_{12}$ catalyst was investigated. The maximum selectivity to aldehyde was found at 120 °C. Supported $Ru_3(CO)_{12}/Co_2(CO)_8$ catalysts have increased activity and selectivity to aldehyde [57]. Heterogeneous catalysts prepared from octacarbonyl dicobalt and alkaline earth oxides were found to be efficient in vapor-phase hydroformylation of ethene and propene [58]. ^{13}C solid-state NMR technique with high-power H decoupling was employed to study heterogenized hydroformylation catalysts containing the anchored complexes of general composition $\equiv Si{-}P_2Co_2(CO)_{6,7}$ and $\equiv Si{-}P_2Co_2(CO)_{7,8}$ (where $\equiv Si{-}P_2$ is the diphosphine ligand covalently bonded to silica surface). The values of chemical shift anisotropy provide information on the molecular motion of anchored metal carbonyl fragments. Evidence was presented for the fast restricted motion of these fragments. The interactions of CO, H_2 and ethene with the anchored cobalt and palladium–cobalt carbonyl complexes were studied to identify the species which might act as intermediates in hydroformylation reaction [59]. Hydroformylation of mono and multiple unsaturated fatty acid derivatives with heterogenized cobalt carbonyl and rhodium carbonyl catalyst was described [60].

Hydroformylation of methyl methacrylate was studied using a silica-supported poly-γ-amino propylsiloxane–rhodium–cobalt bimetallic complex catalyst. The catalyst shows high stability during the reaction and could be used repeatedly. High conversion (95.6%) and selectivity (92.8%) for the normal aldehyde methyl β-formylisobutyrate was observed [61].

The rhodium(I) complex $[Rh(COD)Cl]_2$, intercalated into montmorillonite was found to be an effective catalyst for the selective hydroformylation of allyl acetate derivatives to produce the corresponding linear or branched aldehydes. Linear aldehydes were obtained with high selectivity at temperatures > 130 °C, while the branched aldehyde could be obtained as the major product at lower temperature (<50 °C), and in excellent yield [62]. Improved regioselectivity in hydroformylation of 1-hexene has been achieved by zeolite-encapsulated rhodium(I) species. The linear:branched ratio can be increased by as much as 10 times [63].

The structure and catalytic activity in gas-phase olefin hydroformylation of tetrarhodium clusters coordinated with tris(hydroxymethyl)phosphine (THP) grafted onto silica surfaces were studied. EXAFS and IR spectroscopy has revealed that the number of tris(hydroxymethyl)phosphine ligands coordinating to the tetrarhodium cluster depends on the loading of THP. Tetrarhodium clusters on silica loaded with 6.2 wt% THP are coordinated by two THP ligands and show much higher catalytic activity in hydoformylation reactions than that of monosubstituted clusters of THP/SiO_2 obtained with 1.6 wt% loading or of $Rh_4(CO)_{10}(THP)_2$ in solution [64]. The vapor-phase hydroformylation of ethylene and propylene using rhodium complexes adsorbed on activated carbon and rhodium complexes intercalated in zirconium phosphonates was studied [65].

The ion pairs $RhCl_3$/Aliquat 336® and $RhCl_3.[Me_3N(CH_2)_3Si(OMe)_3]Cl$ entrapped in SiO_2 sol–gel matrices were used among others as olefin hydroformylation catalysts. The immobilized ion pair proved to be stable, leach-proof and recyclable. In comparison with the homogeneous $RhCl_3$/Aliquat 336 catalyst, the immobilized catalysts proved to be superior in most cases [66].

Hydroformylation of propene to butyraldehydes over supported aqueous phase rhodium catalysts was studied in a fixed-bed reactor-GC system. The effects of process parameters such as the ratio of ligand/rhodium, types of support, reaction pressure and temperature, and the water content in the feed stream were investigated [67].

Trans-$[(RhCp^*CH_3)_2(\mu\text{-}CH_2)_2]$ (Cp* = pentamethylcyclopentadienyl) was chemically attached to inorganic oxides such as SiO_2, Al_2O_3, TiO_2 and MgO to prepare rhodium dimer catalysts for ethene hydroformylation. The SiO_2-attached rhodium dimer showed highest activity and selectivity for the hydroformylation [68].

An efficient and reusable polystyrene-supported η^5-cyclopentadienyl rhodium catalyst precursor **46** was prepared and used for the synthesis of substituted cyclopentanones either via hydrocarbonylative cyclization starting from 1,4-dienes or from allylvinyl ethers via tandem Claisen rearrangement and intermolecular hydroacylation of the 4-pentanal intermediates [69].

P = polymer support,

$L_2 = (CO)_2$; 1,5-cyclooctadiene

46

The influence of Li^+, Na^+, K^+ and Zn^{2+} on silica supported cluster anion $[Rh_{12}(CO)_{30}]^{2-}$ catalysts in ethylene hydroformylation has been studied. The selectivity for propanal formation was found to depend on the countercation in the following order: Zn > K ≥ Li ≥ Na. The unpromoted system, prepared from $Rh_4(CO)_{12}$ is less selective [70].

Supported aqueous-phase catalysts for the rhodium-based hydroformylation of methyl methacrylate were found to show much higher activities than those observed under comparable homogeneous and biphasic conditions [71].

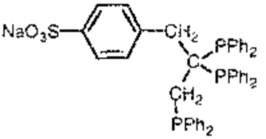
Liquid phase hydroformylation of ring substituted styrenes catalyzed by Rh–B and Rh–Zn–B systems was characterized by ESCA, XRD and FT-IR spectroscopy. Both catalyst were found to be active in the liquid phase hydroformylation of ring substituted styrenes at 80 °C and 100 bar $CO/H_2 = 1$, rhodium/olefin molar ratio 1.5×10^{-3}. No leaching of the catalyst was observed. The chemoselectivity was close to 100%, and the regioselectivity appeared to be controlled by the nature of the ring substituents [72].

See also Refs. [75,103].

1.2.2. Biphasic systems

A high efficiency low pressure hydroformylation process for higher molecular weight olefins has been developed using rhodium/ionic phosphine catalysts. Catalyst solubilization in the non-polar reactants and products is achieved using solubilizing agents, such as *N*-methylpyrrolidone, yielding single-phase systems. Separation of catalyst from product is induced by the addition of small amounts of water outside the hydroformylation reactor. Under the two-phase conditions, most of the catalyst components are found in the polar *N*-methylpyrrolidone/water phase, and the products (aldehydes, olefins, reaction byproducts) in a separate, non-polar, phase. The catalyst phase is recycled to the reactors after thorough drying to ensure a single homogeneous phase at reaction conditions. Traces of catalyst and solubilizing agent are effectively recovered from the product and recycled. A major advantage of this process, over water-based two-phase systems, is the high catalytic reactivity as well as the concomitant high olefin efficiency (>90%) which is achieved with olefins of low water solubility [73].

Zwitterionic rhodium(I) complexes (sulfos)Rh(COD) and $(sulfos)Rh(CO)_2$ (sulfos = **47**) in liquid biphasic catalysis were described for the hydroformylation of 1-hexene, leading to C- alcohols in an alcohol–hydrocarbon system and C- aldehydes in an alcohol–water–hydrocarbon system. All rhodium is recovered in the polar phase at the end of the catalytic reaction [74].



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Three approaches to catalytic hydroformylation involving water soluble ligands, some modified cyclodextrines as ligand, and reactions in an aluminophosphate cavity have been described [75]. Solvent free biphasic hydroformylation of various water-insoluble terminal olefins was achieved in high yields and selectivities by using a water-soluble rhodium/triphenylphosphine trisulfonate catalyst and per(2,6-di-*o*-

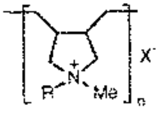
methyl)-β-cyclodextrin as inverse phase transfer catalysts. The catalytic activities were up to ten times higher than those observed without per(2,6-di-*o*-methyl)-β-cyclodextrin [76].

The new ligands obtained by sulfonation of 2,2′-bis(diphenylphosphinomethyl)-1,1′-binaphthalene and 3,4-dimethyl-2,5,6-triphenyl-1-phosphanorborna-2,5-diene were tested for catalytic activity toward hydroformylation of propene. The reported data of the new water-soluble phosphines represent the best results so far recorded in the rhodium-catalyzed hydroformylation of propene [77]. The hydroformylation of 1-pentene to hexanals was studied using Rh(acac)$(CO)_2$ in the presence of triphenylphosphine and sodium salts of monosulfonated and trisulfonated triphenylphosphine in liquid 1,3-dialkylimidazolium salts and a water two-phase system [78].

The catalytic activity of the water-soluble rhodium complex $HRh(CO)(DPM)_3$ ($DPM = Ph_2P(m\text{-}C_6H_4SO_3K)$) in styrene hydroformylation was studied in a biphasic system. Under the conditions of 90 °C, 50 bar syngas, V_{water}/V_{olefin} ratio = 2 and reaction for 3 h, 97.8% conversion of styrene and 94.1% aldehyde yield with 1.5 *iso*/normal ratio were observed [79,80].

Water-soluble rhodium carbonyl complexes with nonionic complex ligands prepared by ethoxylation of tris(*p*-hydroxyphenyl)phosphine were successfully used in the two-phase hydroformylation of higher-molecular-weight olefins at 100–130 °C [81]. Thermoregulated phase-transfer catalysis of hydroformylation of 1-hexene was carried out without water as solvent in the presence of a $RhCl_3$–$P[p\text{-}C_6H_4O(CH_2CH_2O)_nH]_3$ catalyst system [82]. The surface active water soluble phosphine, $P[p\text{-}C_6H_4O(CH_2CH_2O)_nH]_3$, ($n = 4$), was used to generate an aqueous rhodium catalyst for the hydroformylation of 1-dodecene. At 100 °C, 50 bar $CO/H_2 = 1$, pH = 6.5 and 4 h reaction time, 96.0% conversion of 1-dodecene and 84.0% yield of aldehyde (*n*/*iso* = 1.8) was achieved [83].

The influence of the composition of the aqueous phase on the catalytic properties of rhodium(III) chloride modified by polyelectrolytes **48** was studied.



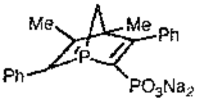
R = Me, X = Cl
R = H, X = H_2PO_4

48

The rate of hydroformylation was found to increase with increasing pH of the aqueous phase. Addition of NaCl, Na_2SO_4 or Na_3PO_4 dramatically changes the catalytic properties. Increasing the anion charge of the added electrolyte increases the stability of the catalytic system [84].

The hydroformylation of propylene to butyraldehyde in the presence of water-soluble rhodium catalysts was studied [85]. An aqueous phase hydroformylation rhodium catalyst was prepared on the basis of polyethylene glycol functionalized by phosphine groups [86].

In the biphasic rhodium-catalyzed hydroformylation of 1-hexene the ligands **49** and **50** at 80 °C, 20 bar $CO/H_2 = 1$, in a water–toluene system gave 66% and 89% yield of aldehyde, *n*/*iso* = 1 and 0.88, respectively [87].



49

50

The effects of reaction temperature, phase transfer agent and the concentration of rhodium catalyst were examined in the catalytic hydroformylation of dicyclopentadiene using a water-soluble rhodium phosphine complex in a two-phase system [88].

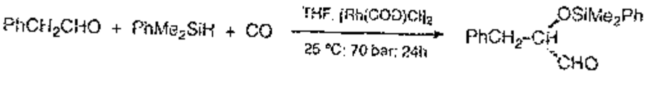
The kinetics of biphasic hydroformylation of 1-octene were studied in the presence of ethanol cosolvent, using the water-soluble $[Rh(COD)Cl]_2$–TPPTS (TPPTS = trisodium salt of trisulfonated triphenylphosphine) complex as a catalyst. The rate of hydroformylation was found to be first order with respect to both catalyst and olefin concentrations and fractional order with respect to dihydrogen concentration. The rate versus carbon monoxide concentration passed through a maximum, indicating a negative order dependence at higher pressures. The results were interpreted on the basis of a well-known hydroformylation mechanism, assuming the rate-determining addition of the olefin to the active catalyst [89,90].

See also Refs. [3,71].

2. Hydroformylation related reactions of CO

2.1. *Silylformylation, hydrocarboxylation, alkoxycarbonylation and amidocarbonylation*

The rhodium complex-catalyzed silylformylation of aldehydes was studied in THF solution at 25 °C and 3–100 bar of carbon monoxide pressure using $PhMe_2SiH$ as the silane reagent leading to the best results [91], e.g.



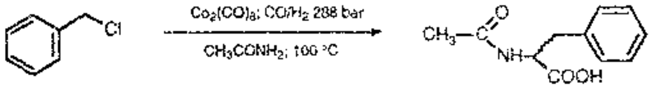
$$PhCH_2CHO + PhMe_2SiH + CO \xrightarrow[25\ ^{\circ}C;\ 70\ bar;\ 24h]{THF,\ [Rh(COD)Cl]_2} PhCH_2\text{-}CH(OSiMe_2Ph)(CHO)$$

80%

The interconversions between zwitterionic and cationic rhodium(I) complexes as catalysts in hydroformylation, silylformylation and hydrogenations have been studied by NMR spectroscopy [92].

The hydrocarboxylation of ethylene to propionic acid was investigated. The best results were achieved by using $RhCl_3 \cdot 3H_2O$ as the catalyst precursor and iodoethane as the promoter at 192 °C and 120 bar $CO:C_2H_4 = 2:1$ pressure [93]. Catalytic double carbonylation of diiodomethane in triethylorthoformate in the presence of a homogeneous rhodium complex was achieved at 120 °C and 100 bar carbon monoxide partial pressure to give diethylmalonate in up to 68% yield [94].

The amidocarbonylation of benzyl chloride with acetamide to obtain *d,l*-*N*-acetylphenylalanine (**51**) has been explored.



51

The best result (82% yield of **51**) was achieved by using methyl *iso*butyl ketone as the solvent and $NaHCO_3$ as an additive. Amidocarbonylation of benzyl alcohol gave **51** in only 8% yield [95].

See also Ref. [46].

2.2. *Water–gas shift reaction and reduction with CO or CO + H_2O*

Liquefaction of Yallourn, Wyoming, Wandoan and Illinois No. 6 coals was studied using water and carbon monoxide as a hydrogen source and iron pentacarbonyl with sulfur as catalyst precursor. The liquefaction of Yallourn coal at 375 °C for 60 min at 70 bar (cold) carbon monoxide pressure results in 95.6 wt% coal conversion with an oil yield of 37.0 wt%. The oil yield further improves in a two-stage liquefaction procedure (60 min at 375 °C and another 60 min at 425 °C) to 55.8 wt% [96].

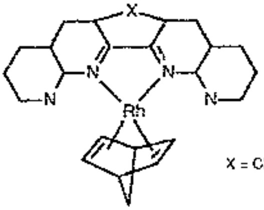
Tetracarbonylrhodate either as K^+, Cs^+ or PPN^+ ($PPN^+ = (PPh_3)_2N^+$) was found to be a very active catalyst for the reduction of nitrobenzene to aniline by CO/H_2O in water as solvent at 60 bar and 200 °C. The reaction is selective for the nitro group [97]. Reductive carbonylation of aromatic dinitro compounds such as 1,4-dinitrobenzene, 1,3-dinitrobenzene and 2,4-dinitrotoluene to afford valuable dicarbamates was found to proceed at 135 °C and 60 bar carbon monoxide pressure with reasonable rates and with high selectivities under the influence of a $Rh(phenanthroline)_2(triflate)_2$ catalyst in combination with an aromatic carboxylic acid as cocatalyst [98].

Interconverting reactions of Ru(0), Ru(I) and Ru(II) carbonyl complexes, together with Ru(II) hydrido carbonyls formed in an acidic solution of $Ru_3(CO)_{12}$ were studied in order to produce H_2 and CO_2 from H_2O and CO [99].

The water–gas shift reaction and the selective reduction of nitrobenzene to aniline under water–gas shift reaction conditions were found to be effectively catalyzed by cationic rhodium(I) complexes such as **52** [100].

The catalytic system $PdCl_2(PPh_3)_2$–HCl in dioxane was found to be highly active and selective at 90 °C and 30 bar carbon monoxide pressure in the hydrogen transfer reaction from H_2O–CO to $PhCOCH_2CH(OH)COOH$ which yields the corresponding γ-keto acid $PhCOCH_2CH_2COOH$ [101].

The complex $[Pt_{15}(CO)_{30}]^{2-}[MV]^{2+}$ (MV^{2+} = methyl viologen cation) encapsu-



$X = CH_2CH_2, CH_2CH_2C$[illegible], [illegible]Me_2

52

lated in the ordered mesoporous channels of FSM-16 (FSM = folded-sheet mesoporous material) was found to exhibit remarkably high activity in the water–gas shift reaction at 27°C [102].

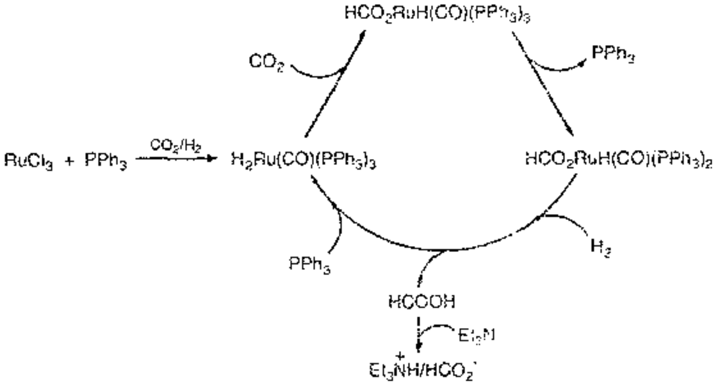
2.3. *Reduction of CO and CO_2*

SiO_2-supported heteronuclear metal carbonyl complexes (dppe)Rh(μ-CO)$_2$M(CO)$_3$ (M = Cr, Mo, W) were used as catalysts for carbon monoxide hydrogenation and hydroformylation of propene. The catalytic activities and selectivities were determined. High activity and selectivity of oxygenates for carbon monoxide hydrogenation was found under atmospheric pressure and 240°C [103].

Based on simple stoichiometric organometallic reactions a new catalytic cycle was proposed, the "alkenyl" mechanism, for methylene polymerization, which occurs during the heterogeneously catalyzed hydrogenation of carbon monoxide. Initiation occurs by coupling of surface methyne and methylene to give the surface vinyl. This then undergoes chain growth by reaction with surface methylene to give surface allyl. The allyl isomerizes to alkenyl which in turn homologates with more methylene. Termination is by reaction of the alkenyl with surface hydride, giving the alkene directly [104].

Addition of weak Brönsted acids such as 1-propanol, 2-pyrrolidone and CF_3CH_2OH was found to improve the turnover numbers in the electrochemical reduction of carbon dioxide to carbon monoxide by iron(0) porphyrins [105]. Electrocatalytic reduction of carbon dioxide to formic acid and carbon monoxide by mixed-metal trimetallic complexes of the form $\{[(bpy)_2Ru(BL)]_2IrCl_2\}^{5+}$ (bpy = 2,2′-bipyridine, BL = 2,3-bis(2-pyridyl)quinoxaline or 2,3-bis(2-pyridyl)-benzoquinoxaline) was investigated. It was found that controlled potential electrolysis using these new trimetallic catalysts can give current efficiencies as high as 99% for CO production with high turnover numbers. This is in marked contrast to the lower current efficiency achieved using the monometallic $[Ir(BL)_2Cl_2]^+$ analogs which produce formate as a reduction product [106].

Hydrogenation of carbon dioxide with dihydrogen in the presence of ruthenium chloride or ruthenium complexes was studied. Ruthenium(III) chloride was found to be an active catalyst precursor at 60 bar $CO_2/H_2 = 1/1$ and at 60°C in the presence of triphenylphosphine and triethylamine to produce 40 mol formic acid/mol ruthenium/hour [107].



The anionic ruthenium complex $[Ru(CO)_3Cl_3]^-$ was found to catalyze the formation of methyl formate from carbon dioxide, dihydrogen and methanol at 60 bar and 160°C in the presence of a strong base such as potassium methylate [108].

The crystal structure of $[Ru(bpy)_2(CO)(\eta^1\text{-}C(O)OH)]^+$ (bpy = 2,2′-bipyridine) as a key intermediate in CO_2/CO conversion has been determined and compared with that of $[Ru(\eta^1\text{-}CO_2)(bpy)_2CO]$. The molecular structure of $[Ru(bpy)_2(CO)(\eta^1\text{-}C(O)OH)]$ has revealed that protonation of $[Ru(\eta^1\text{-}CO_2)(bpy)_2CO]$ shortens the Ru–C(O)OH bond distance compared with the Ru–CO_2 one due to enhancement of dπ–dπ* interaction in the former [109].

Rapid, selective and high-yield hydrogenation of CO_2 can be achieved if the carbon dioxide is in the supercritical state. Thus, it was found that dissolving dihydrogen, a tertiary amine, a catalyst precursor such as $RuH_2[P(CH_3)_3]_4$ or $RuCl_2[P(CH_3)_3]_4$, and a promoter such as water, methanol or DMSO in supercritical carbon dioxide at 50°C leads to the generation of formic acid with turnover frequencies up to or exceeding 4000 h^{-1}. In general, experiments in which a second phase was formed by one or more reagents or additives had lower rates of reaction. The high rate of reaction is attributed to rapid diffusion, weak catalyst solvation and the high miscibility of dihydrogen in supercritical carbon dioxide [110].

The nature of the catalytically active intermediate formed in situ from the tetrameric cluster $[\{(COD)Rh(\mu\text{-}H)\}_4]$ and the bidentate phosphine $Ph_2P(CH_2)_4PPh_2$ during hydrogenation of carbon dioxide to formic acid was investigated by kinetic measurements and by NMR spectroscopy [111].

Highly active catalysts for the hydrogenation of carbon dioxide to formic acid in DMSO/NEt_3 were formed in situ from $[\{(COD)Rh(\mu\text{-}Cl)\}_2]$ and various monodentate or bidentate ligands with phosphorus as the donor atom. Thus, formic acid concentrations up to 2.3 ± 0.2 M can be obtained in less than 6 h at ambient temperature under a total initial pressure of 40 bar by using rhodium concentrations of 5×10^{-3}M [112]. The SiO_2-supported heterobinuclear metal complexes, $(PPh_3)_2HPt(\mu\text{-}PPh_2)M(CO)_4$ and $(dppe)Rh(\mu\text{-}CO)_2M(CO)_3$ (M = Cr, Mo, W; dppe = $Ph_2PCH_2CH_2PPh_2$) were found to be highly active and selective catalysts for carbon dioxide hydrogenation [113].

3. Reviews

(1) Asymmetric catalytic reactions such as hydrogenation, hydroformylation, oxidative carbonylation, hydrocyanation and hydrovinylation for practical synthesis of bio-active substances. A review with 61 references [114].

(2) Carbonylation by complex catalysts. A review with more than 24 references among others on the hydroformylation and silylformylation of olefins. Recent results of branching-selective and asymmetric hydroformylation are described. Commercial processes of hydroformylation using water-soluble organo-phosphines are discussed [115].

(3) Some β-dicarbonyl rhodium complexes functioning as a precursor of homogeneous active catalyst for hydrogenation, selective hydroformylation, gas were summarized. A review with 129 references [116].

(4) The research: "Facile catalyst separation without water: fluorous biphase hydroformylation of olefins" of I.T. Horváth and J. Rábai is reviewed with commentary (10 references) [117].

(5) Hydroformylation of simple olefins catalyzed by metals and clusters supported on unfunctionalized inorganic carriers were reviewed (more than 123 references) [118].

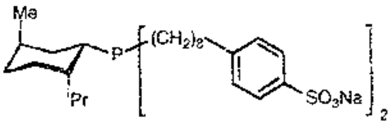
(6) A review of applications of organometallic chemistry in the petroleum refining and petrochemical industry, among others about hydroformylation products propanol and butanol/butyraldehyde (80 references) [119].

(7) Supported aqueous-phase catalysts. A review with 9 references on immobilization of homogeneous metal complex catalysts on solid supports in hydroformylation of 1-octene and asymmetric hydrogenation of an acrylic acid [120].

(8) Catalytic conversions in water: environmentally attractive processes employing water-soluble transition metal complexes. A review with 65 references discussing among others hydroformylation of propene in a two-phase system (Ruhrchemie/Rhone Poulenc process) and hydroformylation of higher olefins in a two-phase system [121].

(9) A review, with 15 references, of the synthesis and aggregation of water-soluble phosphines **53** and **54** and the hydroformylation catalytic activity of rhodium complexes of the phosphines as compared to that of rhodium complexes of $P(C_6H_4SO_3Na)_3$ [122].

(10) Models for supported aqueous-phase catalysis. A review, with 11 references, on immobilized homogeneous catalysts on solid supports for use in aqueous phase in olefin hydroformylation [123].



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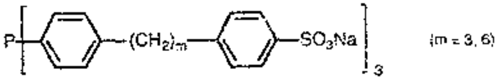

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(11) Homogeneous catalysis by noble metal complexes. A review, with 7 references, among others on rhodium-catalyzed olefin hydroformylation [124].

(12) Molecular metal carbonyl clusters and volatile organometallic compounds for tailored mono and bimetallic heterogeneous catalysts. A review, with 36 references, among others of ethylene hydroformylation using silica supported $[Rh_{12}(CO)_{30}]^{2-}$ as precursor [125].

(13) Virtually no environmental impact: the biphasic oxo process. A review with 24 references. The survey reviews 10 years of experience of the Ruhrchemie/Rhone–Poulanc process, using $RhH(CO)[P-(3-C_6H_4SO_3Na)_3]_3$ catalyst, dissolved in water [126].

(14) Potential energy surfaces of transition-metal-catalyzed chemical reactions. A review with 94 references among others on the $RhH(CO)_2(PR_3)_2$-catalyzed olefin hydroformylation cycle [127].

(15) Asymmetric hydrosilylation and hydroformylation reactions. A review with greater than 29 references [128].

(16) Macromolecular metal complexes as catalysts with improved stability. A review with 25 references on polymer-bound tertiary amine–copper complexes and polymer-bound phosphite–rhodium complexes as catalysts for oxidative coupling of phenols and hydroformylation of alkenes, respectively [129].

(17) Metal-catalyzed hydroformylations. A review with 24 references on potentialities and limits of hydroformylations and similar reactions [130].

(18) Catalytic production of dimethylformamide from supercritical carbon dioxide. Methyl formate synthesis by hydrogenation of supercritical carbon dioxide in the presence of methanol. Selectivity for hydrogenation or hydroformylation of olefins by hydridopentacarbonylmanganese(I) in supercritical carbon dioxide. A review with commentary and 1 reference about the title research of P.G. Jessop et al. [131].

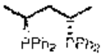
(19) A review of the selective catalytic reduction of aromatic nitro compounds into aromatic amines, *iso*cyanates, carbamates and ureas using carbon monoxide (greater than 127 references) [132].

(20) The organometallic chemistry of carbon dioxide. A review with more than 111 references [133].

Table 1
Metal index

Metal	References
Zr	[51,52,65]
Cr	[103,113]
Mo	[103,113]
W	[103,113]
Mn	[131]
Fe	[81,99,109]
Ru	[49,57,99,106–110,132]
Co	[1–7,9,50,57–61,95]
Rh	[10–48,50–52,60–74,76–94,97,98,100,103,111–113,121–127,129,132]
Ir	[106]
Ni	[2]
Pd	[46,53,54,59,101,132]
Pt	[46,55,56,102,113]
Zn	[70,72]
Sn	[53–56]

4. List of abbreviations

Ac	acetyl
acac	acetylacetonate
(+)-BDPP	
bpy	2,2′-bipyridine
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
DMF	*N,N*-dimethylformamide
DMSO	dimethylsulfoxide
dppb	$Ph_2PCH_2CH_2CH_2CH_2PPh_2$
dppe	$Ph_2PCH_2CH_2PPh_2$
ee	enantiomeric excess
py	pyridine
RT	room temperature
TPPTS	trisodium salt of the trisulfonated triphenylphosphine
wt%	weight percent

The metals and their associated references are given in Table 1.

Acknowledgements

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