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Application of transition metals in hydroformylation. Annual survey covering the year 1999

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Contents

Abstract

Hydroformylation in homogeneous and heterogeneous systems, and hydroformylation related reactions of carbon monoxide reported in 1999 are reviewed. © 2001 Elsevier Science B.V. All rights reserved.

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

Homogeneously catalyzed propene hydroformylation in supercritical carbon dioxide using $Co_2(CO)_8$ precatalyst was studied in batch reactors. The experiments were carried out at 68–108°C and 90.6–194.1 bar. It was found that the product selectivity at a fixed temperature increased with pressure, and at a fixed pressure it decreased with temperature. Chemical equilibrium calculations showed that the changes in selectivity were not equilibrium controlled [1].

Supercritical water (374°C and 220.5 bar) has been used as a solvent to achieve homogeneous oxo synthesis and other reactions such as hydrogenation of the aldehyde products and the water–gas shift reaction in the presence of $Co_2(CO)_8$, $[Co(CO)_3PPh_3]_2$, and $Rh_6(CO)_{16}$ as the precatalysts [2].

The effect of the number of metal atoms in clusters of rhodium and cobalt on the catalytic olefin hydroformylation properties have been discussed [3].

The rate of cobalt-catalyzed hydroformylation of cyclohexene to cyclohexanecarboxaldehyde was found to be significantly reduced when xenon is added to the reaction mixture at a concentration similar to that of the olefin. No significant effect was found by using helium or neon under similar conditions [4].

The hydroformylation of 1-pentene was studied using $RhCl(PPh_3)_3$ and $Co_2(CO)_8$ modified by different trialrylstibines. It was found that using the triarylstibine and catalyst precursor in a 1:1 molar ratio increases the yields of aldehydes. The maximum yield of aldehydes obtained were 98.6% with $n/\text{iso} = 2.4$ when the $RhCl(PPh_3)_3$ + trimesitylstibine system were used and 85.0% with $n/iso = 3.4$ when $Co_2(CO)_8$ + trimesitylstibine system was applied [5].

Activities of 3-pyridyldiphenylphosphine-substituted rhodium(I) and cobalt(0) carbonyl complexes were tested in hydroformylation of 1-hexene [6].

The effect of reaction parameters in the unmodified cobalt-catalyzed hydroformylation of technical methylpentenes has been studied. The optimum reaction conditions leading to the highest selectivity towards aldehydes are: 130°C, 0.08–0.1% cobalt concentration and 2.2–2.4 h reaction time [7].

1.1.2. Rhodium catalysts

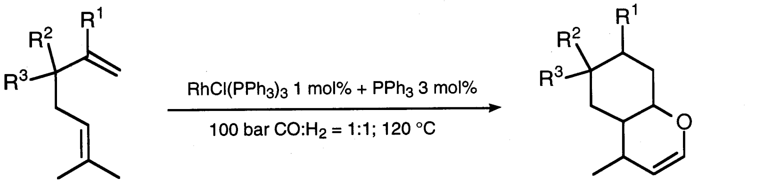
The β-regioselective hydroformylation of 2-phenylpropene, 2-methylpropene, and 2,3,3-trimethylbutene was investigated via deuterioformylation at 100°C and 100 bar, using $Rh_4(CO)_{12}$ as the catalyst precursor. At partial substrate conversion the crude reaction mixtures were analyzed by ^2H NMR. The conclusion from the results is that the primary rhodium-alkyl intermediate undergoes migratory insertion on carbon monoxide, leading to the corresponding linear aldehyde. On the other hand, the tertiary rhodium-alkyl intermediate, which forms in the case of 2-phenylpropene and 2-methylpropene but not in the case of 2,3,3-trimethylbutene, undergoes β-hydride elimination exclusively. Both conclusions are in accord with the observed almost complete β-regioselectivity [8].

The kinetics of the homogeneous catalytic hydroformylation of cyclohexene to cylohexanecarboxaldehyde was studied using high pressure in situ infrared (IR) spectroscopy. Starting with $Rh_4(CO)_{12}$ as the catalyst precursor in *n*-hexane as solvent at 25°C, $P(H_2) = 20$ bar and $P(CO) = 60$ bar at four different rhodium concentrations a pseudo steady state was found between the species $Rh_4(CO)_{12}$ and $C_6H_{11}CORh(CO)_4$. Regression of the kinetic data indicates that there is no statistically significant contribution to aldehyde formation from a catalytic binuclear elimination mechanism. All aldehyde formation can be accounted for in terms of the hydrogenolysis of acylrhodium tetracarbonyl with dihydrogen as the rate-limiting step [9]. Detailed kinetics of the unmodified homogeneous rhodium-catalyzed hydroformylation of styrene have been studied using $Rh_4(CO)_{12}$ as the catalyst precursor in *n*-hexane solution. Quantitative high-pressure in situ IR spectroscopic measurements were made under isobaric and isothermal conditions in the range of $T = 298$–313 K, $P(H_2) = 0.27$–1.01 MPa, $P(CO) = 3.0$–6.0 MPa, $[Rh_4(CO)_{12}]_0 = 3.5 \times 10^{-5}$–$1.7 \times 10^{-4}$ mol fraction, and $[\text{styrene}] = 0.119$–0.349 mol fraction. The disappearance of the precursor $Rh_4(CO)_{12}$ resulted in the formation of two observable acyl intermediates: $(\pm)$-$PhCH(CH_3)CORh(CO)_4$ (major isomer) and $PhCH_2CH_2CORh(CO)_4$ (minor isomer). The disappearance of $Rh_4(CO)_{12}$ follows the rate expression: $\text{rate} = k_0^1[Rh_4(CO)_{12}]^{1.0}[CO]^{1.3}[H_2]^{0.9}[\text{styrene}]^{0.15}$, where $k_0^1 = (\kappa T/h)\exp(-62.6\ \text{kJ/(mol RT)} + 37.2\ \text{J/(mol K R)})$. The formation of the major product follows the rate expression: $\text{rate} = k_0^2[Ph(CH(CH_3)CORh(CO)_4]^{1.0}[CO]^{-1.0}[H_2]^{1.0}[\text{styrene}]^{0.0}$, where $k_0^2 = (\kappa T/h)\exp(-78.8\ \text{kJ/(mol RT)} + 15.2\ \text{J/(mol K R)})$. The corresponding expressions for the minor product are: $\text{rate} = k_0^3[PhCH_2CH_2CORh(CO)_4]^{1.0}[CO]^{-1.0}[H_2]^{1.0}[\text{styrene}]^{0.0}$, where $k_0^3 = (\kappa T/h)\exp(-113\ \text{kJ/(mol RT)} - 102\ \text{J/(mol K R)})$. The ratio of branched acyl to linear acyl complex at 30°C is ca. 15:1. Because the efficiency of the linear aldehyde producing cycle is higher, the observed selectivity for the major branched aldehyde over the minor linear aldehyde is ca. 10:1 [10].

The homogeneous catalytic hydroformylation of 20 alkenes such as, e.g. 1-decene, 5-decene, 2-methyl-2-heptene, and methylenecyclopentane was studied starting with $Rh_4(CO)_{12}$ as the catalyst precursor in *n*-hexane as solvent, using high-pressure in situ IR spectroscopy as the analytical tool. Typical reaction conditions were $T = 293$ K, $P(H_2) = 20$ bar, $P(CO) = 20$ bar, $[\text{alkene}]_0 = 0.1$–0.02 mol fraction and $[Rh_4(CO)_{12}]_0 = 6.6 \times 10^{-5}$ mol fraction. The $\nu(C{\equiv}O)$ and $\nu(C{=}O)$ bands of the acylrhodium tetracarbonyls have been determined. The approximate turnover frequencies for these systems were also evaluated. Higher turnover frequencies were found for the acyl complexes formed at primary carbon atoms [11]. This is just the opposite of that observed in the case of styrene [9].

3,3-Bis(*p*-fluorophenyl)propanal has been obtained in $> 99\%$ selectivity by the rhodium-catalyzed hydroformylation of 1,1-bis(*p*-fluorophenyl)ethene [12]. Rhodium-catalyzed regioselective hydroformylation of cinnamaldehyde acetals were reported [13]. Rhodium-catalyzed hydroacylation by RhCl(COD)(dppe) was applied in the synthesis of spiro[4.5]decane-1,6-dione [14].

A one-pot preparation of substituted hexahydro-4H-chromenes via rhodium-catalyzed tandem hydroformylation starting from 1,5-dienes has been described. The multi-step procedure starts with hydroformylation of one double bond followed by carbonyl-ene reaction, a second hydroformylation and enol ether forming cyclization [15]. For example:



R^1 = Me, R^2,R^3 = H 21% yield

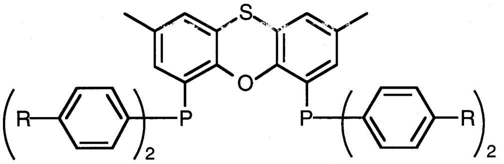
R^1 =H, R^2,R^3 = Me 40% yield

Rhodium carbonyl complexes formed from rhodium(III) chloride hydrate modified by poly-*N*,*N*-dimethyl-*N*,*N*-diallylammonium chloride in a methanol–chloroform medium in the hydroformylation of 1-hexene were studied by in situ IR spectroscopy. Along with the hydridocarbonyl rhodium complexes, anionic complexes of the $[Rh(CO)_2Cl_2]^-$ type were detected [16].

High-pressure IR spectroscopic studies of rhodium complexes containing thiolate bridge ligands revealed the presence of mononuclear rhodium hydride species under hydroformylation conditions (80°C, 5–30 bar). The activities using these systems as catalyst precursors in 1-hexene hydroformylation were fully accounted for by the mononuclear species observed [17].

The tetranuclear early-late heterobimetallic ($TiRh_3$) complexes $[CpTi(\mu^3\text{-}S)_3\{Rh(diolefin)\}_3]$ (diolefin = COD, tetrafluorobenzobarrelene) in the presence of P-donor ligands were found to be active catalyst precursors in the hydroformylation of 1-hexene and styrene under mild reaction conditions. Thus, hydroformylation of 1-hexene gives 96% conversion to aldehydes and 77% regioselectivity for *n*-heptanal at 80°C and 5 bar $CO:H_2 = 1:1$ pressure in the presence of PPh_3 ($P/Rh = 2–4$). Under similar conditions (10 bar) hydroformylation of styrene gives 70% conversion and 88% regioselectivity in favor of 2-phenylpropanal [18].

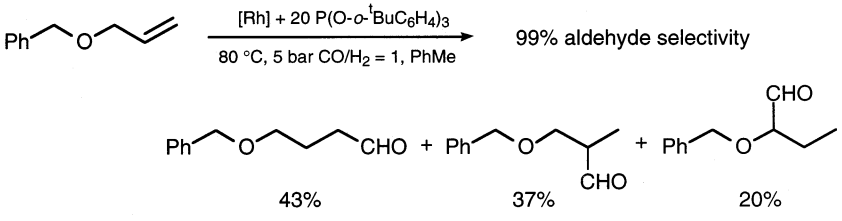
The electronic effect of thixantphos ligands (**1**) in the rhodium diphosphine-catalyzed hydroformylation of 1-octene and styrene was investigated. It was found that an increase in the linear:branched ratio and catalytic activity goes with decreasing phosphine basicity. IR and NMR spectroscopy showed that the (diphosphine)$Rh(CO)_2H$ complexes consist of dynamic equilibria of diequatorial (ee) and equatorial-apical (ea) isomers. The ee:ea isomer ratio shifts gradually from almost one for the $N(CH_3)_2$-substituted ligand to more than nine for the CF_3-substituted ligand. These results indicate that the chelation mode in the (diphosphine)$Rh(CO)_2H$ complexes per se is not the key parameter controlling the regioselectivity [19].

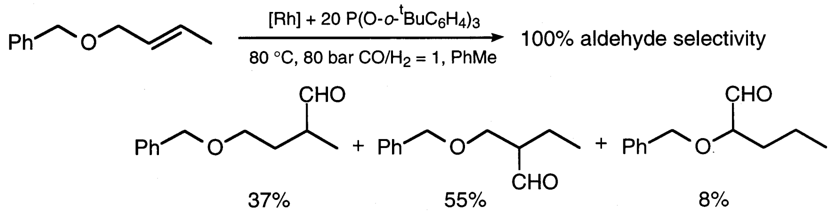


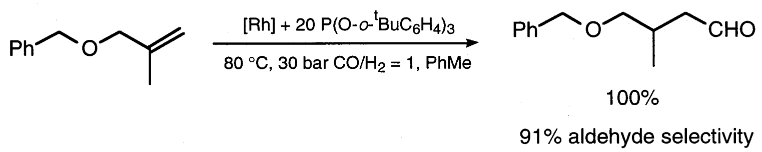
(R = $N(CH_3)_2$, OCH_3,
H, F, Cl, CF_3.)

1

Hydroformylation of different allyl benzyl ethers to the corresponding γ-, β-, and α-hydroxyaldehydes in the presence of $[\mathrm{Rh}(\mu\text{-}\mathrm{S(CH_2)_3NMe_2})(\mathrm{COD})] + \mathrm{PR_3}$ (R = Ph, O-*o*-^{t}BuC$_6$H$_4$) as the catalyst precursors was studied. High yields but low regioselectivities were obtained in the hydroformylation of allyl benzyl ether and benzyl butenyl ether. Excellent yield and regioselectivity was achieved in forming 4-benzyloxy-3-methyl-butanal starting from benzyl-2-methallyl ether [20]. For example:

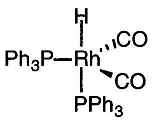






The catalytic activity and selectivity of in situ generated heterodonor phosphine-rhodium catalysts were tested in the hydroformylation of methyl methacrylate at 100°C and 60 bar. An exceptionally high selectivity to methyl 2-formylbutyrate was observed with [*o*-(methylthio)phenyl]diphenylphosphine ligand, which gave a branched to normal ratio of about 27 [21].

High-pressure IR studies of rhodium complexes containing thiolate bridge ligands have been made under hydroformylation conditions (80°C and 5–30 bar). Thus, the catalyst systems $[\mathrm{Rh_2\{\mu\text{-}S(CH_2)_3NMe_2\}_2(COD)_2}]/\mathrm{PR_3}$ (R = Ph, OPh), $[\mathrm{Rh_2\{\mu\text{-}S(CH_2)_3S\}(COD)_2}]_2/\mathrm{PPh_3}$, $[\mathrm{Rh_2\{\mu\text{-}S(CH_2)_4S\}(COD)_2}]/\mathrm{PPh_3}$, $[\mathrm{Rh_2\{\mu\text{-}XANTOSS\}(COD)_2}]_2/\mathrm{PPh_3}$ (XANTOSS = 9,9-dimethylxanthene-4,5-thiolate), and $[\mathrm{Rh(acac)(CO)_2}]/\mathrm{PR_3}$ (R = Ph, OPh) revealed the presence of mononuclear rhodium hydride species **2** and **3**.



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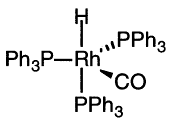
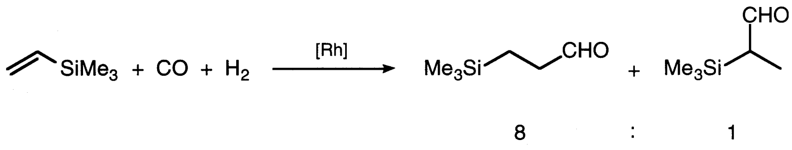
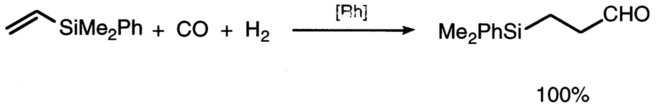


3

The activities and selectivities obtained during the hydroformylation of 1-hexene using these systems as catalyst precursors, can be fully accounted for by the mononuclear species observed. Results of deuterioformylation experiments also support the conclusion that mononuclear species formed under hydroformylation conditions are most probably responsible for the activity of the catalyst [22].

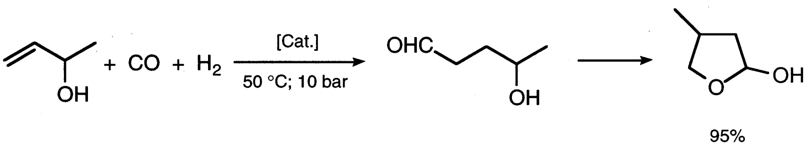
The catalytic system composed of Rh(acac)$(CO)_2$ as catalyst precursor with a small excess of free *N*-pyrrolylphosphine ($[P(NC_4H_4)_3]$:[Rh] = 3–10 was found to be very active in hydroformylation of vinylsubstituted silanes at 80°C and 10 bar $CO/H_2 = 1$ [23]. For example:



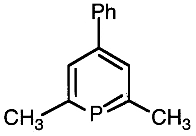


The homogeneous hydroformylation of styrene catalyzed by dihydridorhodium complex RhH_2(1,3-diphenyltriazene)$(PPh_3)_2$ in DMSO was reported. The effect of reaction conditions on the ratio of 2- and 3-phenylpropanal was investigated [24].

The catalytic system containing Rh(acac)$(CO)_2$ and water soluble phosphine, $Ph_2PCH_2CH_2C(O)NHC(CH_3)_2CH_2SO_3Li$ has been used for the hydrogenation and hydroformylation of 1-buten-3-ol, 2-methyl-2-propen-1-ol, and 2-buten-1-ol in water. The main products of the hydroformylation at 50–80°C and 10 bar $CO/H_2 = 1$ are 2-hydroxytetrahydrofuran derivatives formed by cyclization [25]. For example:



Strong π-acceptor ligands, phospha-π-aromatic compounds, pyrrolyl phosphines, and phosphenium cations were evaluated for rhodium-catalyzed hydroformylation of styrene. Among the monodentate ligands tested, the *ortho*/*ortho'*-disubstituted phosphabenzene derivative **4** provided a rhodium-catalyst with the relative highest catalytic activity. Among the bidentate ligands tested, an oxazoline/phosphabenzene system **5**, which is capable of forming an eight-membered chelation ring gave the best results [26].



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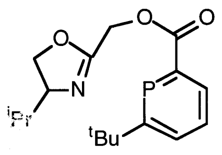
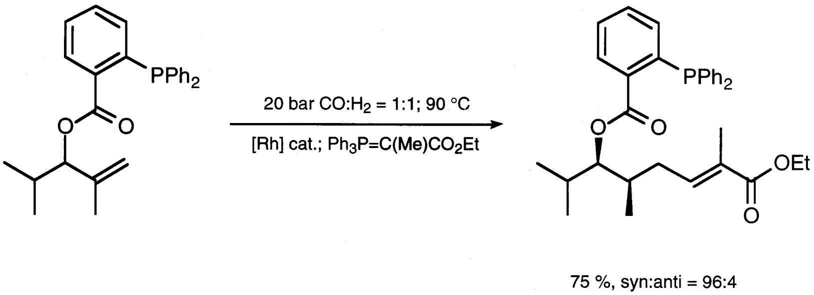
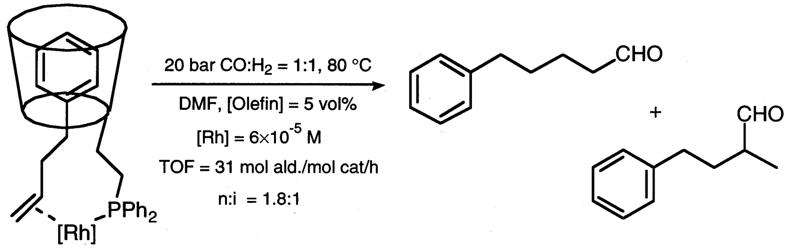


5

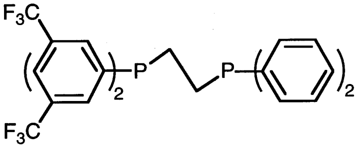
The stereoselective rhodium-catalyzed hydroformylation of methallylic alcohols was applied using the substrate-bound catalyst-directing *ortho*-diphenyl-phosphanylbenzoyl group in synthesis of polyketide natural products [27]. Hydroformylation of methallyl-*o*-diphenylphosphanylbenzoic acid esters in the presence of 1.1 equivalents of the stabilized disubstituted Wittig ylide $Ph_3P{=}C(Me)CO_2Et$ gave the reaction product of the aldehyde formed by hydroformylation with the ylide in a one-pot procedure in good yield and diastereoselectivity [28]. For example:



β-Cyclodextrin monophosphinite combined with $[Rh(COD)Cl]_2$ was found to give a catalyst that exhibits substrate selectivity in hydroformylation of certain C_8 and C_{10} olefins due to the inclusion of substrates in the cyclodextrine cavity [29].



Electrically dissymmetric DIPHOS derivatives such as **6**–**9** were found to give higher *n*:*iso* regioselectivity in rhodium-catalyzed hydroformylation of 1-hexene than either of their symmetric counterparts at 36°C under 6 bar of H_2:CO = 1:1 using 0.2 mol% $Rh(CO)_2(acac)$:diphosphine = 1:1 catalyst precursor. In model (diphosphine)$Ir(CO)_2H$ complexes of dissymmetric diphosphines **6**–**9** two apical-equatorial chelate isomers **10** and **11** were observed in rapid interconversion at room temperature (r.t.). Low temperature ^{31}P NMR characterization in each case has shown that the equatorial phosphine of the major isomer (96–60%) has electron-withdrawing aryl substituents. This result supports the hypothesis that an electron-withdrawing aryl substituent on an equatorial phosphine increases the *n*:*iso* ratio in hydroformylation while an electron-withdrawing substituent on an apical phosphine decreases the *n*:*iso* ratio [30].



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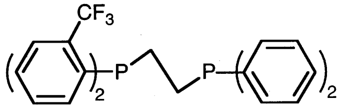

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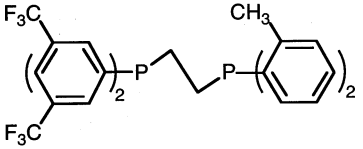

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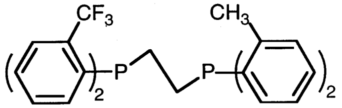

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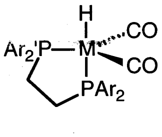

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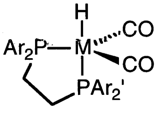
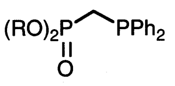


11

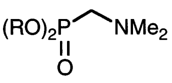
Rhodium complexes with the bidentate ligand 2-diphenylphosphino-phenolate were not found to be suitable catalyst precursors for 1-hexene hydroformylation at 80°C and 10 bar $CO:H_2 = 1:1$ because the chelate ring formed with the ligand is too stable and in most cases prevent the formation of the catalytically active rhodium hydride species [31].

Various bifunctional, potentially hemilabile ligands bearing phosphorus groups such as **12** and **13** were prepared and their rhodium complexes were tested in hydroformylation of styrene. At 25°C and 40 bar $CO:H_2 = 1:1$ using $[Rh(COD)Cl]_2$ and **13** as the catalyst precursor, in 15 h, 67% conversion of styrene and 99% aldehyde selectivity was achieved [32].



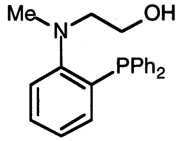
(R = Et, ^{i}Pr)

12



13

Two new cationic rhodium(I) complexes containing a phosphino amino alcohol **14** ligand and a methoxy amino phosphine **15**, respectively, have been used as catalyst precursors in the hydroformylation of styrene. At 40–60°C and 100 bar $CO/H_2 = 1$ pressure a quantitative chemoselectivity for aldehydes with a very good regioselectivity (89–94%) for the branched aldehyde was observed [33].



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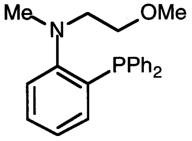
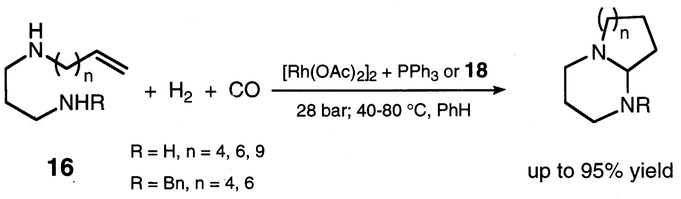


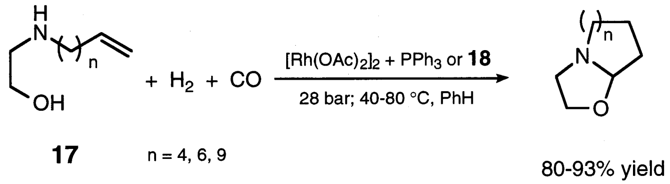
15

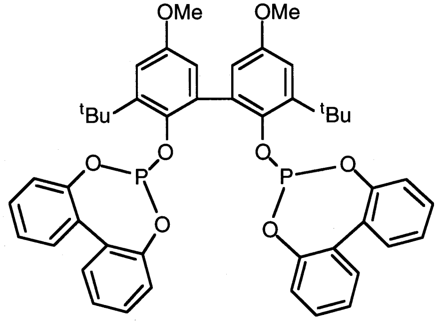
Olefins such as allyl alcohol, propene, 1-hexene, styrene, methyl acrylate and acrolein were hydroformylated with formaldehyde as the source of CO and H_2 in the presence of $RhH(CO)(PPh_3)_3$ to form aldehydes. 4-Hydroxybutanal is formed in 26% yield as a major product from the reaction of allyl alcohol with formaldehyde under a dinitrogen atmosphere at 100°C [34].

The influence of phosphine and phosphite ligands and the P/Rh molar ratio on the catalytic properties of rhodium carbonyl complexes in the hydroformylation of 2-butenes was studied [35]. Hydroformylation of styrene and 1-octene using binuclear and oligomer rhodium(I) complexes as precatalysts containing the bis-*p*-phosphinito ligand $[(p\text{-}Ph_2POC_6H_4)_2X]$ ($X = O$, CMe_2, S) was studied. Almost quantitative conversion of styrene was achieved with the catalytic system formed by $[Rh(acac)(CO)_2]$ and $(p\text{-}Ph_2POC_6H_4)_2CMe_2$ in a 1:0.5 molar ratio, operating at 60°C and 40 bar $CO{:}H_2 = 1{:}1$ pressure, and leading to a 82:18 ratio of $PhCH(CH_3)CHO$ over $PhCH_2CH_2CHO$ [36].

Cyclic amines with medium and large ring sizes have been obtained in up to 85% yield in one-pot rhodium-catalyzed reactions of aminoalkenes with H_2/CO [37]. A series of *N*-alkenyl-1,3-diaminopropanes (**16**) and *N*-alkenylaminoethanols (**17**) were allowed to react with H_2/CO in a PPh_3- or BIPHEPHOS (**18**)-modified rhodium-catalyzed reaction to give diazabicycloalkanes and oxazabicycloalkanes containing medium or large rings in excellent yields [38].

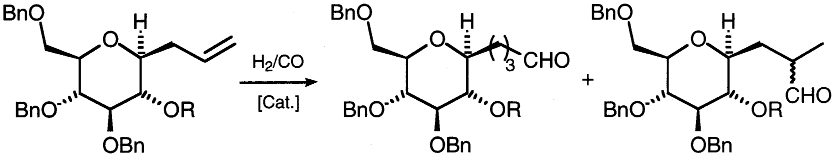






18

Rhodium-catalyzed hydroformylation of glucose derivatives **19** and **20** at 80°C and 27 bar H_2:CO = 1:1 in ethyl acetate using **18** as a ligand led to regiospecific formation of the linear aldehyde, while using PPh_3 as ligand gave a mixture of linear and branched aldehydes [39].

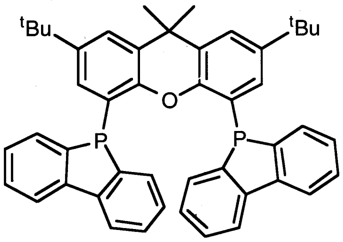


19 R = Bn

20 R = H

Fluorinated and chlorofluorinated norbornenenes and their analogs were hydroformylated in the presence of (acetylacetonato)dicarbonylrhodium-triphenylphosphine as the catalyst precursor to give regioisomeric *exo* aldehydes with the CHO group at the 2- or 3-position. Conversions from 80 to 97%, and selectivities close to 100% were found [40].

New dibenzophospholyl- and phenoxaphosphanyl-substituted xanthene ligands **21** and **22** were found to exhibit high activity and selectivity in the rhodium-catalyzed hydroformylation of 1-octene, and unprecedented high activity and selectivity in the hydroformylation of *trans*-2- and *trans*-4-octene to linear nonanal. Thus, 1-octene gave at 80°C and 20 bar CO:H_2 = 1:1 using Rh:P:1-octene = 1:10:673, 65–68 linear:branched aldehyde product with 83–86% selectivity. 2-Octene and 4-octene gave, at 120°C and 2 bar CO:H_2 = 1:1, a linear:branched ratio of nonanals up to 9.5 and 6.1, respectively [41].



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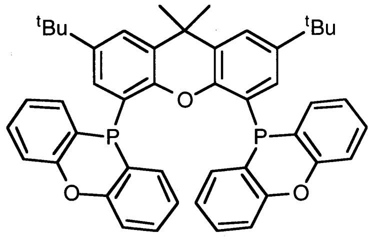


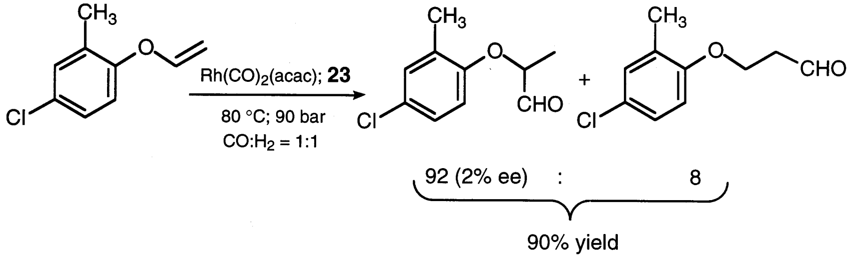
22

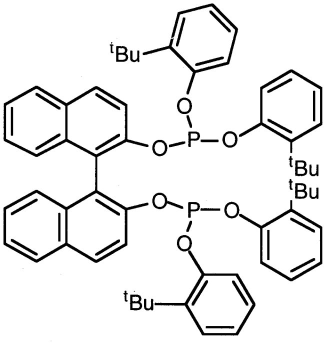
The rhodium-catalyzed hydrocarbonylation of isopropylallylamine and *n*-butylallylamine was studied in the presence of PPh_3 and diphosphine ligands. The best yields of the desired *N*-isopropyl- and *N*-*n*-butyl-butyrolactam was obtained using the PPh_3-based catalyst in 57 and 73% yield, respectively at 70°C and 20 bar CO:H_2 = 4:1 in THF [42].

A new method to recycle homogeneous catalysts from monophasic reaction mixtures by using an ionic liquid exemplified for the rhodium-catalyzed hydroformylation of methyl-3-pentenoate has been described [43].

Stereoselectivities of rhodium catalysts containing C_2-symmetric diphosphine ligands have been calculated with a combined quantum mechanical–molecular mechanical method [44].

Enantioselective hydroformylation of aryl vinyl ethers bearing various substituents in the aromatic ring was studied using rhodium(I) complexes with diphosphites and commercially available ferrocenylphosphines at 80°C and 90 bar $CO:H_2 = 1:1$. In most cases high chemo- and regioselectivities towards the formation of the desired branched aldehyde are achieved ($> 80\%$). The enantioselectivities are generally low ($\leq 10\%$) [45]. For example:





23

The structure–activity relationship for chelating phosphite ligands used in rhodium-catalyzed hydroformylation of 1-octene has been obtained. Using a simplified kinetic model the relative rate constants for linear and branched aldehyde formation were determined and compared with results of molecular modeling. The energy differences obtained with molecular modeling were plotted against the energy differences obtained from kinetic experiments and a linear correlation was found [46]. The kinetics of ethene hydroformylation with triphenylphosphine-modified rhodium catalyst in tetraethyleneglycol dimethylether were investigated. At $P/Rh > 3$ and $[PPh_3] > 50$ mmol l^{-1} at 100°C the rate of ethene hydroformylation was found to be first order in both rhodium and ethene concentration. The combination of low phosphine and high olefin concentration, however, leads to a saturation in ethene. Both carbon monoxide and triphenylphosphine inhibit the reaction above a threshold value, while below the threshold a positive kinetic effect exists. Dihydrogen concentration has little effect on the rate of hydroformylation. Under typical hydroformylation conditions (100°C, 10 bar $H_2/CO = 1$, $[Rh] = 0.146$ mmol l^{-1}, $[PPh_3] = 254$ mmol l^{-1}) the selectivity for propionaldehyde is nearly 100%. The ethane formation is low (0.2–0.4 mol%) and was found to be a function of the $P(H_2)/P(CO)$ ratio. Based on a refined Wilkinson mechanism, a kinetic model was developed which fits all experimental observations and can be used to predict reaction rates and selectivities over a wide range of reaction conditions [47].

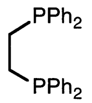
Hydroformylation of 1-octene in supercritical carbon dioxide in the presence of $RhH(CO)[P(p\text{-}CF_3C_6H_4)_3]_3$ as the catalyst precursor was studied. The incorporation of *p*-(trifluoromethyl)-groups in the conventional hydroformylation catalyst, $RhH(CO)(PPh_3)_3$, provided enhanced solubility in supercritical carbon dioxide while maintaining catalyst activity and selectivity in hydroformylation. The rate of hydroformylation was found to show a first-order dependence on $RhH(CO)[P(p\text{-}CF_3C_6H_4)_3]_3$ concentration. The total system pressure has no effect on either the reaction rate or selectivity. However, the selectivity was found to depend on the catalyst concentration [48]. Kinetics of hydroformylation of 1-octene in supercritical carbon dioxide using $HRh(CO)[P(p\text{-}CF_3C_6H_4)_3]_3$ as the catalyst was investigated at 50°C and 273 bar pressure. Through a nonlinear least-squares fitting routine the following rate expression was determined to be the best fit: $r_{1\text{-octene}}$ (in mol dm^{-3} min) $= 6.2[H_2]^{0.48}[HRh(CO)[P(p\text{-}CF_3C_6H_4)_3]_3]^{0.84}[1\text{-octene}]^{0.50}/1 + 0.69[CO]^{2.2}$, yielding an average absolute error of 15.5%.The observed kinetic behavior differs significantly from the behavior of systems employing the nonfluorinated analog $HRh(CO)(PPh_3)_3$, in organic solvents. The most significant differences are the ~ 0.5 order in $[H_2]$, the lack of substrate inhibition, and the absence of a critical catalyst concentration [49].

The effect of ligand modification on the activity of rhodium-catalyzed 1-octene hydroformylation in supercritical carbon dioxide has been studied at 50°C and 273 bar pressure. The activity of the rhodium catalyst formed in situ from $Rh(CO)_2(acac)$ and L (L = tertiary arylphosphine) increased with decreasing basicity of the phosphine according to the series: $P(3,5\text{-}(CF_3)_2C_6H_3)_3 > P(4\text{-}CF_3C_6H_4)_3 \approx P(3\text{-}CF_3C_6H_4)_3 > P(4\text{-}CF_3OC_6H_4)_3 > P(4\text{-}F(CF_2)_4(CH_2)_3C_6H_4)_3$. Good correlation was observed between activity and carbonyl stretching frequency for the rhodium complexes $HRh(CO)L_3$ [50].

The kinetics of hydroformylation of styrene using $HRh(CO)(PPh_3)_3$ as the catalyst precursor were investigated in the temperature range 60–80°C. First order with respect of both rhodium and dihydrogen was observed. The initial rate of hydroformylation is independent of the styrene concentration. Carbon monoxide has a negative effect on the rate of the reaction. The activation energy was found to be 68.8 kJ mol^{-1} [51].

The effect of the excess of ligand and the chelate ring size on the selectivity of rhodium–diphosphine-catalyzed styrene hydroformylation was investigated [52]. A combined QM/MM method was used for the determination of regioselectivities in rhodium–phosphine-catalyzed olefin hydroformylation. Tendencies in experimentally found regioselectivities of four systems with the bidentate chelating ligands

DIPHOS (**24**), BISBI (**25**), NAPHOS (**26**), and the monodentate reference ligand triphenylphosphine could be reproduced [53].



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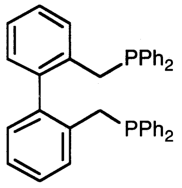

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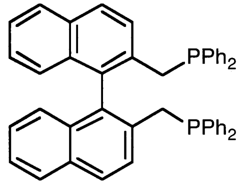
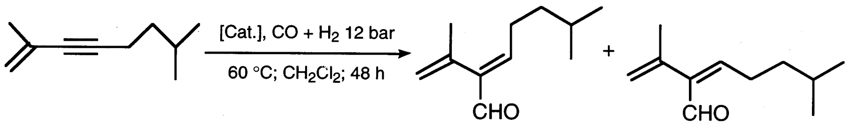


26

The viability of the concept of dual catalytic systems for consecutive isomerization–hydroformylation reactions in hydroformylation of internal olefins to linear aldehydes has been demonstrated by a ruthenium/rhodium catalyst system with chelating phosphanophosphite ligands [54].

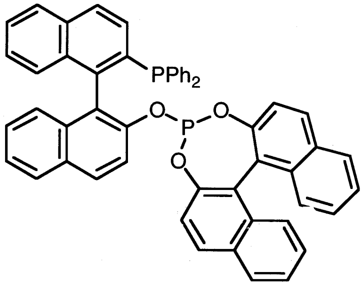
Hydroformylation of aliphatic enynes catalyzed by a zwitterionic rhodium complex and triphenylphosphite has been studied. Thus, the reaction of aliphatic 1-en-3-ynes with CO and H_2 in the presence of $(\eta^6\text{-}C_6H_5BPh_3)^-Rh^+(1,5\text{-COD})$ and $P(OPh)_3$ affords dienes in high stereoselectivity in moderate to good yields [55]. For example:



55% 5%

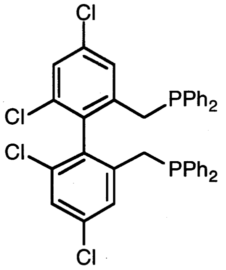
The hydroformylation of 1-octene in supercritical carbon dioxide was studied by using online-gas chromatography monitoring. The influences of reaction parameters such as temperature, synthesis gas pressure, and P/Rh ratio on reaction rates and selectivities were found to be grossly similar to the effects observed in conventional solvents. With unmodified catalysts, the hydroformylation is faster in supercritical carbon dioxide than in organic solvents or liquid carbon dioxide under otherwise identical conditions. Modified catalytic systems formed with perfluoralkyl-substituted triarylphosphine and triarylphosphite ligands give a *n*/*iso* ratio of 5–6. Olefin isomerization is effectively suppressed in supercritical carbon dioxide [56]. The rhodium-catalyzed hydroformylation of simple alkenes and the cyclohydrocarbonylation of amino and hydroxy dienes in supercritical carbon dioxide were investigated [57].

Catalytic asymmetric hydroformylation of styrene using $Rh(acac)(CO)_2$/BINAPHOS (**27**) as the catalyst precursor was studied in the presence of compressed carbon dioxide. Under conditions close to the critical data of pure carbon dioxide 66% ee was obtained, but very low ee values were found at high carbon dioxide densities [58].



27

The new axially chiral diphosphine ligands (±)-**28**, (−)-**28** and the uniform sulfonated derivative of (±)-**28** were tested in homogeneous, asymmetric, and biphase rhodium-catalyzed hydroformylation of styrene, respectively, and the results were compared to those obtained with BISBI (**29**) and sulfonated BISBI. The comparison with BISBI shows high similarity in all cases with respect to both activity and selectivity for the favored hydratropaldehyde. The activity of sulfonated **28** is somewhat lower than that of sulfonated BISBI. Using (−)-**28** at temperatures up to 40°C, an enantiomeric excess of 15% of (*S*)-hydratropaldehyde was observed (substrate/rhodium ratio = 300; ligand/rhodium ratio = 2; 50 bar H_2:CO = 1:1; 16 h) [59].



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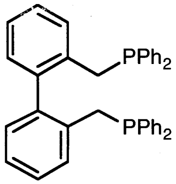
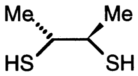


29

The asymmetric hydroformylation of styrene has been investigated using rhodium(I) complexes with chiral dithiolate ligands from **30** and **31**. The observed chemoselectivity, regioselectivity, and enantioselectivity has been related to the catalyst structure [60].



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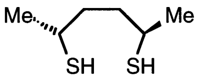
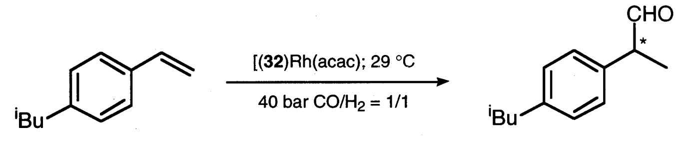
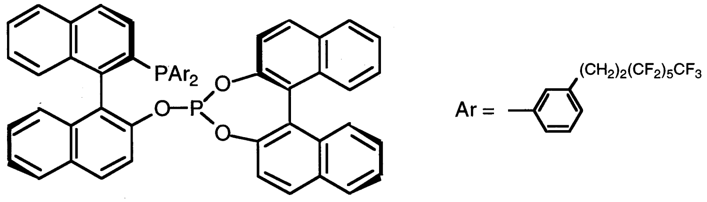


31

By the use of the rhodium complex [(**32**)Rh(acac)] as the catalyst precursor in supercritical carbon dioxide in asymmetric hydroformylation of styrene and *para*-substituted styrenes, very high regioselectivities and excellent enantioselectivities were obtained [61]. For example:



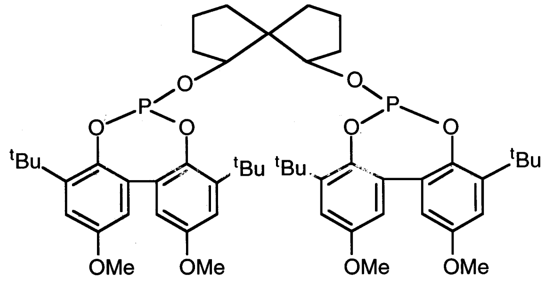
96% regioselectivity
92.8% ee (R)



32

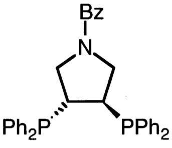
Rhodium-BINAP-catalyzed asymmetric hydroformylation has been used in the synthesis of (3*S*,4*S*)-[(*R*)-1′-(*tert*-butyldimethylsilyl)oxyethyl]-4-[(*R*)-carboxyethyl]-2-azetidinone [62].

Asymmetric hydroformylation of vinylacetate in the presence of BINAP–modified rhodium(I) catalyst gave up to 99% regioselectivities with up to 60% ee of the product [63]. Chiral diphosphites and phosphinite-phosphites derived from spiro[4.4]nonene-1,6-diol were tested in rhodium-catalyzed asymmetric hydroformylation of styrene. The best results, 97% regioselectivity and 65% ee, have been obtained using a rhodium complex with the ligand **33** having a (1*R*,5*R*,6*S*)-*cis*,*trans*-spirol backbone [64].



33

Rhodium-catalyzed hydroformylation of styrene was investigated using the diphopsphine **34** as ligand. The results were compared with those of the rhodium–$PEtPh_2$ catalyst. The observed less than 4% ee of the (*S*)-isomer of 2-phenylpropanal was related to the presence of a catalytically-active species in which the diphosphine **34** coordinates each rhodium in a monodentate mode [65].

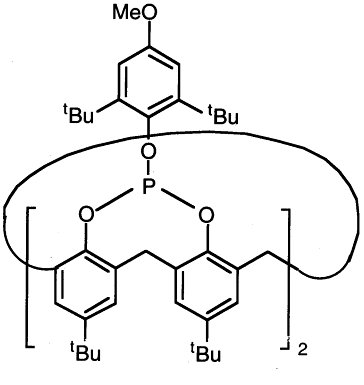


34

Binuclear rhodium complexes [$Rh_2(\mu$-RiSS$)(COD)_2$] and [$Rh_2(\mu$-XySS$)(COD)_2$] (RiSSH$_2$ = 1,2-*O*-isopropylidene-3,5-dithiol-α-D-ribofuranose, XySSH$_2$ = 1,2-*O*-isopropylidene-3,5-dithiol-α-D-xylofuranose) have been used as catalyst precursors in hydroformylation of styrene. At 75°C and 30 bar CO:H$_2$ = 1:1 pressure in THF in the presence of PPh$_3$ (PPh$_3$:Rh = 1:1), > 99% chemoselectivity for aldehydes and 89% regioselectivity in 2-phenylpropanal was observed. Comparison of the results with those obtained with [$Rh(acac)(CO)_2$] as the precatalyst complex led to the conclusion that mononuclear rhodium carbonyl species are responsible for the catalytic activity in the case of the binuclear complexes [66].

Cationic rhodium complexes with macrocyclic diphosphines as chiral ligands has been used as catalysts in asymmetric hydroformylation of styrene. At 30 bar CO:H$_2$ = 1:1 pressure and 65°C, > 92% regioselectivity in 2-phenylpropanal but low (0–12%) ee was obtained [67]. 5,17-Bis(*tert*-butyl)-11,23-bis(diphenylphosphinomethyl)-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]arene combined with [RhCl(norbornadiene)]$_2$ was used as catalyst precursor in styrene hydroformylation at 70°C and 40 bar CO:H$_2$ = 1:1 with styrene/Rh ≈ 585 in the presence of NEt$_3$. Linear and branched aldehydes were obtained in a 9:91 ratio [68].

Hydroformylation of 1-octene with [$Rh(CO)_2(acac)$] and chelated bisphosphites with a calix[4]arene backbone as catalyst precursors at 80–100°C and 5–20 bar CO/H$_2$ = 1/1 gave high (92–96%) nonanal regioselectivities. The catalyst system using ligand **35** showed an exceptional high, 99.5% nonanal regioselectivity [69].



35

See also Refs. [2,3,5,6,72–74,82,83,92,188].

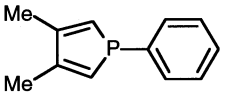
1.1.3. Other metals as catalysts and bimetallic catalysts

Styrene was hydroformylated under 100 bar of $CO:H_2 = 1:1$ at 120°C in the presence of a catalytic amount of $Ru_3(CO)_{12}$ and 1,10-phenanthroline in DMF to give the corresponding aldehydes in 80% yield with an *iso*-selectivity of 72%. With the use of quinuclidine as a ligand in place of 1,10-phenanthroline in *N*,*N*-dimethylacetamide, the corresponding branched and linear oxo-alcohols were obtained in 53% and 28% yields, respectively [70].

The hydroformylation of diphenylacetylene to α-phenylcinnamaldehyde has been achieved using a hydrido triruthenium cluster incorporating the 2-(methylamino)pyridyl group as a hemilabile ancillary ligand. The catalytic cycle were demonstrated on the basis of isolated intermediates [71].

Bimetallic (Rh–W and Rh–Mo) catalytic systems with phosphido bridges have been tested in hydroformylation of styrene, 1-hexene, phosphinoalkenes, N-subtstituted pentenylamines and pentenylamides, and the results were compared to those obtained with $[Rh(OAc)_2]_2/PPh_3$ as precatalyst. The catalysts showed very similar reactivity and selectivity [72].

Hydroformylation of styrene was studied using in situ generated phosphole-modified platinum–tin and rhodium catalysts. A catalyst prepared from $PtCl_2(PhCN)_2$, $SnCl_2$ and **36** gave at 100°C and 40 bar $CO/H_2 = 1/1$ 90% aldehyde selectivity with a 5.9 branched/straight ratio. Rhodium catalysts with phosphole ligands gave almost complete aldehyde selectivity, and the regioselectivity for the branched aldehyde was found to be 80.5% using **37** and 58% using **36** [73].



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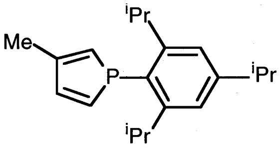
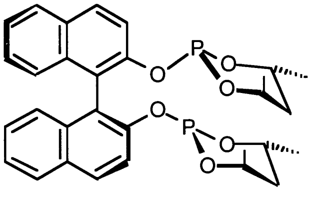


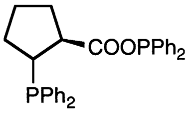
37

Asymmetric hydroformylation of styrene using rhodium and platinum complexes of diphosphites containing atropisomeric backbones and chiral 1,3,2-dioxaphosphorinane moieties was investigated. The maximum enantioselectivity (39% ee) and a remarkable high regioselectivity (84%) towards the branched aldehyde was observed with the platinum system: $Pt(PhCN)_2Cl_2$–$SnCl_2$–**38** at 60°C and 100 bar $CO:H_2 = 1:1$ in CH_2Cl_2 [74].



38

Aminophosphine-carboxyphosphinite diphosphines (**39**–**41**), synthesized from the corresponding α-amino acids were tested among others in the asymmetric platinum-catalyzed hydroformylation of styrene. The branched aldehyde product obtained (2-phenylpropanal/3-phenylpropanal ratio = 65/35) showed less than 5% ee [75].



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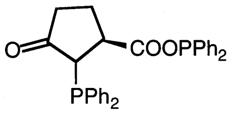

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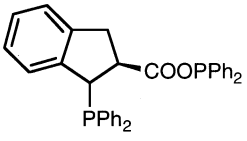
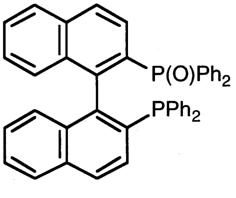


41

The axially chiral phosphinyl phosphine BINAPO (**42**) combined with $PtCl_2(PhCN)_2$ and $SnCl_2$ gave a catalyst for styrene hydroformylation capable to produce up to 30% ee of the prevailing branched aldehyde at 85°C and 90 bar $CO:H_2 = 1:1$ [76].



42

See also Refs. [18,30,54].

1.2. Heterogeneous systems

1.2.1. Supported complexes

Cobalt and ruthenium–cobalt catalysts prepared from $Co_2(CO)_8$ and ionic salts, respectively, were studied in vapor phase hydroformylation and carbon monoxide hydrogenation. Promotion by alkali or alkaline earth cations were found to affect the performance of the $Co_2(CO)_8/SiO_2$ catalyst significantly: the activity decreased in both ethene hydroformylation and carbon monoxide hydrogenation, but at the same time the selectivity for other oxygenates increased. A selectivity of 47% for propanoic acid formation was observed on an alkaline earth oxide promoted $Co_2(CO)_8/SiO_2$ catalyst [77]. Surface-bound $RhCo_3(CO)_{12}/SiO_2$ was prepared by reaction of $Co_2(CO)_8$ and $[Rh(CO)_2Cl]_2$ in the presence of SiO_2 and was found to be active in ethylene hydroformylation [78]. A highly active bimetallic supported rhodium–cobalt hydroformylation catalyst was prepared from $RhCl_3$ and $Co_2(CO)_8$. Catalytic study in steady-state ethylene hydroformylation showed that the catalyst obtained by surface-mediated synthesis of $Rh^+(CO)_2/SiO_2$ from $RhCl_3/SiO_2$, followed by impregnation with $Co_2(CO)_8$ and reduction by dihydrogen at 623

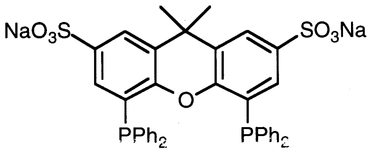
K is more active than a catalyst derived from $RhCo_3(CO)_{12}/SiO_2$ and a catalyst derived by coimpregnation of $[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8$ on SiO_2. This result suggests that the high rhodium dispersion of $[Rh(CO)_2O_{(s)}]_2$ plays a crucial role in the formation of highly dispersed bimetallic rhodium–cobalt sites [79].

Hydroformylation of propene was investigated using rhodium–phosphine complex catalysts supported by carbon nanotubes. It was found that these catalysts give an *n*/*iso* ratio of 12–13 at 120°C and 10 bar propene:CO:H_2 = 1:1:1 pressure with a turnover frequency of 0.12 s^{-1} [80].

Rhodium carbonyl thiolate complexes tethered on silica-supported metal (Pd, Pt, Ru, and Ir) heterogeneous catalysts were found to be active catalysts of olefin (1-octene, styrene) hydroformylation at 60°C and 1 bar CO:H_2 = 1:1 [81].

The heterogenized zwitterionic rhodium(I) complexes (sulfos)Rh(COD) and (sulfos)$Rh(CO)_2$ (sulfos = $^{-}O_3SC_6H_4CH_2C(CH_2PPh_2)_3$) on high surface area silica were found to be reusable catalysts for 1-hexene hydroformylation. The immobilized catalysts show higher chemoselectivity than the unsupported analogous [82].

The water-soluble rigid large bite angle bidentate diphosphine **43** was tested as a rhodium-containing supported aqueous phase catalyst in 1-octene hydroformylation at 80°C and 50 bar CO:H_2 = 1:1. High regioselectivity towards the linear aldehyde (> 90%) was observed in ten consecutive catalytic runs which show no metal leaching [83].



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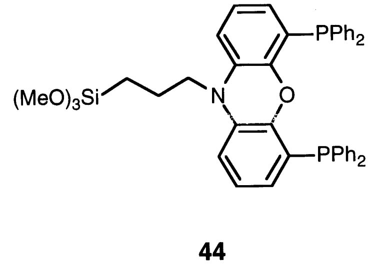
An environmentally benign catalyst for the selective hydroformylation towards linear aldehydes has been described. Thus, the sol-gel immobilized [HRh(siloxantphos)$(CO)_2$] (siloxantphos = **44**) catalyst containing 1×10^{-5} mol rhodium g^{-1} of silica in 1-octene hydroformylation at 80°C and 50 bar CO:H_2 = 1:1 shows a 93% selectivity towards the linear aldehyde, which is similar to the value for the homogeneous catalyzed reaction. No deterioration of the catalytic performance in eight consecutive runs was observed. The decrease in rate in successive catalytic cycles was found to be very small, indicating that the ligand siloxantphos retains the rhodium quantitatively in the solid state [84].



44

Structure and catalytic performance of SiO_2-supported trisulfonated triphenylphosphine trisodium salt (TPPTS)/Rh(acac)$(CO)_2$ catalyst in 1-hexene hydroformylation was investigated. The catalytic activity was found to be promoted when a proper amount of water vapor was introduced into the reactant. According to ^{31}P NMR spectra the amount of the surface complex {Rh(CO)$(TPPTS)_2$ in the catalyst is higher when pre-treatment at 100°C for 2 h under wet syn-gas is applied. This surface complex was found to be the catalytically-active species for olefin hydroformylation [85]. Immobilized trisulfonated triphenylphosphine–rhodium complexes on a high surface area supporter of SiO_2 have been used as supported aqueous-phase catalysts in hydroformylation of propene. At 100–110°C, 200 bar $CO:H_2 = 1:1$, $[Rh] = 7.5 \times 10^{-5}$, and $P/Rh = 25$, the turnover number was found to be in the range of 194–223 g butyraldehyde/(g × Rh × h) and the *n*/*iso* ratio of the butyraldehydes is 14.2 [86]. Tris(sodium-*m*-sulfonatophenyl)phosphine pillared hydrotalcite was prepared, characterized and used as catalyst precursor component in olefin hydroformylation [87].

Diphenylphosphinomethylated polyaminoamido dendrimer-silica supported rhodium(I) complexes were found to be highly active catalysts for the hydroformylation of a variety of olefins. Aryl olefins and vinyl esters afford branched chain aldehydes in high selectivity [88].

4-(4′-Polystyrylmethyloxy)-3-carboxylatomethyloxy-1-phenylacetate bis-*m*-coordinated rhodium(II) diacetate complex, a resin-bound analog of dirhodium tetraacetate, was found to be an efficient, stable and re-usable immobilized alkene hydroformylation and hydrogenation catalyst. Its catalytic activity was demonstrated for the hydroformylation of 1-hexene at 80°C and 40 bar $CO:H_2 = 1:1$. In the presence of some PEt_3 1-hexene gave 100% conversion to aldehydes with an *n*:*iso* ratio of 1:1 [89].

The hydroformylation of 1-hexene was studied using $RhCl(PPh_3)_3$ on modified montmorillonite K as the catalyst. On re-use, the supported species exhibits an increase in activity and selectivity, which was maintained on re-use in up to 15 cycles and rhodium leaching was not detected [90].

Rhodium carbonyl catalysts immobilized on polymeric supports were investigated in the hydroformylation of olefins. Catalysts based on styrene-4-*N*-pyrrolidino-pyridine copolymer and polymeric organosiloxanes as the supports were found to be highly active in hydroformylation of isobutene under conditions, where traditional homogeneous catalysts show no activity [91].

The catalytically-active rhodium thiolate binuclear complex $[Rh_2(\mu\text{-}S(CH_2)_2NHMe_2)(CO)_2(PPh_3)_2]^{2+}$ was used in hydroformylation of styrene in methanol solution and in form of supported catalyst on a cation exchange resin. The metal complex-loaded cationic resin behaved as a multifunctional catalyst. It was active in the hydroformylation of styrene and the subsequent formation of the acetals leading to 1,1-dimethoxy-2-phenylpropane in 85% selectivity. The homogeneous catalyst led to identical selectivity in the branched aldehyde isomer as the immobilized catalyst but about 20-fold faster [92].

Plant fiber support was used in rhodium-catalyzed vapor-phase hydroformylation of ethylene to propionaldehyde at 60–90°C and 40–50 bar syn-gas pressure [93].

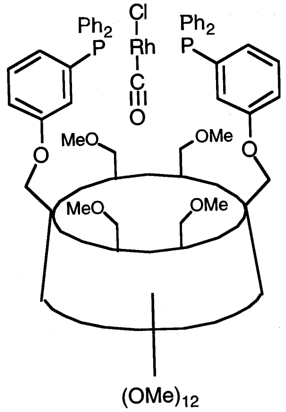
Polymer-immobilized chiral phosphine–phosphite–rhodium(I) complexes were used in asymmetric hydroformylation of styrene, vinyl acetate, (*Z*)-2-butene, and 3,3,3-trifluoropropene. In the case of styrene 84/1689/11 ratios of 2- and 3-phenylpropanal, and 89% (*R*)-enantiomeric excess of 2-phenylpropanal were observed [94]. See also Refs. [98,103,156]

1.2.2. Biphasic systems

Water-soluble and air-stable cluster $Ru_3(CO)_9(TPPMS)_3$ (TPPMS = sodium-*m*-(diphenylphosphino)benzene sulfonate) was found to catalyze the hydroformylation of propene and ethene. The addition of halide promoters enhanced the catalytic activity and in the case of ethene led to the selective formation of 3-pentanone [95].

Hydroformylation of 2-pentenes in an aqueous two-phase system with a cobalt–TPPTS (TPPTS = trisodium salt of the trisulfonated triphenylphosphine) catalyst has been studied. At elevated temperatures and pressures good yields of hexanals were obtained. Linear to branched ratios (*n*:*iso*) of up to 70:30 were observed [96].

Rhodium-capped diphosphino α-cylodextrin (**45**) has been tested in the biphasic catalytic hydroformylation of 1-octene. At 60°C and 40 bar $CO:H_2 = 1:1$ using water:methanol = 6:4, in the presence of **45**, 1-octene was converted with > 99% chemoselectivity into a 70:30 = *n*:*iso* mixture of aldehydes [97].



45

Nitrogen-containing polymer-bound rhodium carbonyl complex catalysts were used in the hydroformylation of 1-hexene and isobutene under conditions of two-phase catalysis (water–organic solvent). Isovaleraldehyde is selectively produced in isobutene hydroformylation [98].

Water-soluble systems based on rhodium complexes and polyelectrolytes in isobutene hydroformylation were studied. These catalytic systems exhibited an unexpectedly high activity under the conditions where homogeneous hydroformylation virtually did not occur in the presence of conventional rhodium catalysts [99]. A water-soluble rhodium complex with tris(hydroxymethyl)phosphine, *cis*-$[RhH_2\{P(CH_2OH)_3\}_4]Cl$, has been used in the hydroformylation of 1-pentene under biphasic conditions. In water–benzene at 100°C and 40 bar $CO:H_2 = 1:1$, 1-pentene was quantitatively converted to hexanal (43%) and 2-methylpentanal (57%) [100].

A series of poly(ethylene oxide)-substituted triphenylphosphines has been used as ligand and phase-transfer catalysts in the rhodium-catalyzed two-phase hydroformylation of higher olefins. A turnover frequency as high as 180 h^{-1} for 1-dodecene has been reported [101].

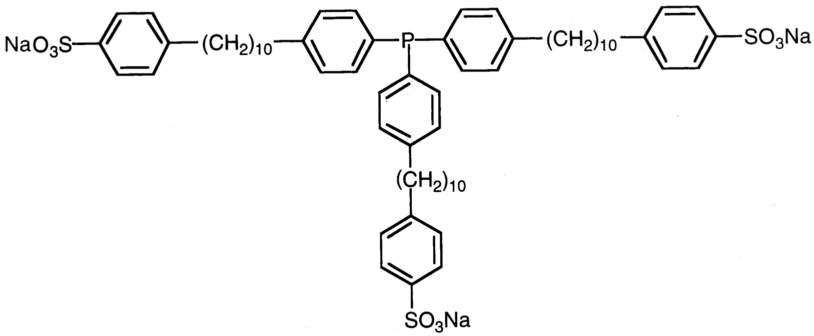
Hydroformylation of 4-isobutylstyrene using aqueous/organic biphasic media and octylpolyglycol-phenylene-phosphite-modified rhodium catalyst has been studied. At 80°C and 40 bar $CO/H_2 = 1$ 99%, aldehyde yield was observed with a molar ratio of branched/normal = 2.5 [102].

Triphenylphosphine chemically bound to water-soluble poly-acrylic acid and poly-ethyleneimine polymers were used as ligands in rhodium-catalyzed biphasic and supported aqueous phase hydroformylation of both propene and 1-octene at 100°C, 5 bar $CO:H_2$:propene = 1:1:1 and 60°C, 40 bar $CO:H_2 = 1:1$, respectively [103].

Catalysts obtained from water-soluble polymer ligands $REPPh_2$, $REOPPh_2$, $(REO)_2PPh$, and $REOP(OPh)_2$ (where $R = BuO$, $E = (CH_2CH_2O)_{111}CH_2CH_2{-}$) and $Rh(acac)(CO)_2$ were found to catalyze the aqueous biphasic hydroformylation of 1-dodecene under mild conditions (50°C, 215 bar $CO:H_2 = 1:1$). The catalytic activity increases in the order: $REOP(OPh)_2 < REPPh_2 < REOPPh_2 < (REO)_2PPh$. The effect of ligand structure, temperature, ligand-to-rhodium ratio, addition of free PPh_3 and $P(OPh)_3$ on catalytic activity and stability has been studied [104].

The effect of sodium sulfate [105] and various metal cations [106] on the hydrogenation of 1-hexene catalyzed by $RhCl(CO)(TPPTS)_2$ in organic/aqueous two-phase systems was studied. It was found that Na_2SO_4 at suitable concentrations can increase the stability of the catalyst in aqueous phase, decrease the leaching of rhodium complexes into the organic phase, and increase the conversion of olefin into aldehyde. The order of influence of the other metal cations in the presence of cetyltrimethylammonium bromide was found to be $Na^+ < K^+ < Li^+ < Zn^{2+} < Mg^{2+} < Ca^{2+} < < Ni^{2+} < Fe^{2+} < Sr^{2+} < Cu^{2+} < Fe^{3+}$, $Al^{3+} < Cr^{3+}$. The effects of anions decrease with the order $SO_3^{2-} > CO_3^{2-} > S_2O_3^{2-} > Cl^- > Br^- > B_4O_7^{2-} > HCO_3^- > I^- > EDTA^{2-} > H_2PO_4^{4-} > SO_4^{2-}$ [107]. The effect of acids and bases on $HRh(TPPTS)_3$ has been studied by ^{31}P and ^{1}H NMR spectroscopy [108]. The micellar effect of different surfactants in $RhCl(CO)(TPPTS)_2$-catalyzed 1-dodecene hydroformylation has been studied. It was found that the formation of micelle was not only favorable for the reaction acceleration, but also favorable for the increase of linear aldehyde ratio in products (up to 6.3 = *n*/*iso*) [109]. The addition of small amounts of triphenylphosphine to either $[HRh(CO)(TPPTS)_3]$ or $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ in order to maintain the active species near the water|toluene interface and to increase the yield in the hydroformylation of 1-octene was examined. NMR studies of the rhodium species present in solution show that using $[HRh(CO)(TPPTS)_3]$ as the catalyst precursor, the main species responsible for the increase in the reactivity is [HRh(CO)(PPh$_3$)$_3$] which operates in the organic phase. From [Rh$_2$(μ-S^{t}Bu)$_2$(CO)$_2$(TPPTS)$_2$] under the same interfacial catalysis conditions [Rh$_2$(μ-S^{t}Bu)$_2$(CO)$_2$(PPh$_3$)$_2$] is irreversibly produced in direct proportion to the amounts of PPh$_3$ added to the system. The PPh$_3$-substituted rhodium complexes are responsible for a substantial leaching of rhodium from the aqueous phase [110,111].

Sulfonated dibenzofuran-based water soluble triphenylphosphine analogs were used as ligands among others in the rhodium-catalyzed two-phase hydroformylation of propene [112]. The new water soluble surface active phosphines **46** and **47** were used for the rhodium-catalyzed hydroformylation of 1-octene and 1-tetradecene at 120°C and 14 bar CO/H$_2$ = 1:1 under two-phase conditions. Rates and selectivities were found to be superior to TPPTS-modified rhodium catalysts under the same reaction conditions [113].



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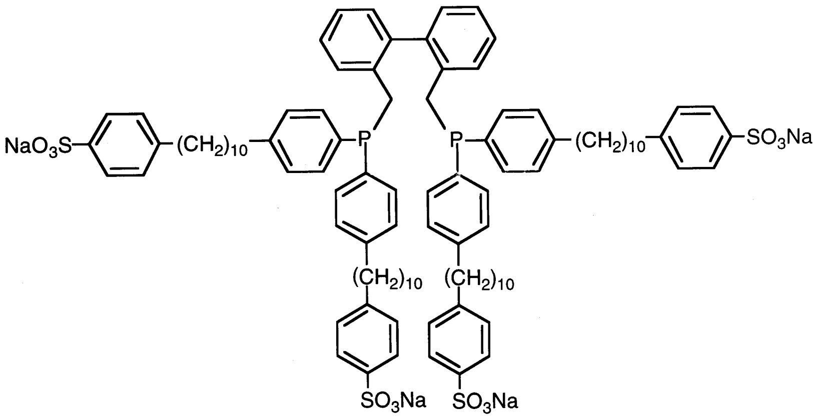


47

Asymmetric hydroformylation of styrene with rhodium complexes of sulfonated diphosphines, (*S*,*S*)-BDPPTS and (*R*,*R*)-CBDTS (BDPPTS = tetrasulfonated 1,2-bis(diphenylphosphino)pentane; CBDTS = tetrasulfonated 1,2-bis(diphenylphosphinomethyl)cyclobutane) was studied in aqueous solutions. Using (*R*,*R*)-CBDTS with the catalyst precursor $[Rh(\mu\text{-}OMe)(COD)]_2$ at 50°C and 14 bar $CO/H_2 = 1/1$, 17% ee in (*S*)-2-phenylpropanal has been achieved [114].

Hydroformylation of olefins between C_6 and C_{16} were studied in reverse micellar systems and compared with hydroformylations in a non-micellar system. Reaction rates and selectivities for aldehydes were found to be higher in the micellar system [115]. Carbohydrate-substituted phosphines as new ligands for two-phase catalysis have been synthesized in which the hydrophilic character of the ligands is attributed to the neutral carbohydrate moiety. Superior catalytic performance was observed, compared to ionic hydrophilic ligands among others in rhodium-catalyzed hydroformylation of higher olefins [116].

Water-soluble rhodium complexes [RhCl(CO)(tpa)] (tpa = 1,3,5-triaza-7-phosphaadamantane) [117], $[RhI(CO)(mtpa^+I^-)_2]$ and $[RhI(CO)mtpa^+I^-)_3 \cdot 4H_2O$ ($mtpa^+I^-$ = 1-methyl-1-azonia-3,5-diaza-7-phosphaadamantane iodide) [117,118] were found to be catalyst precursors in two-phase hydroformylation and hydrocarboxylation of alkenes such as 1-hexene, and show some catalytic activity in water–gas-shift reactions as well.

Biphasic hydroformylation, hydrocarboxylation, and Wacker oxidation of water insoluble olefins were investigated in the presence of chemically modified β-cyclodextrins. In all cases, cyclodextrins were found to be more efficient than common mass transfer promoters in increasing the activity and the selectivity of reactions [119].

The rate of hydroformylation of 1-octene catalyzed by a water-soluble catalyst was measured in a mechanically agitated batch reactor at various stirring speeds and organic phase holdups. The predicted values of the rate were found to be in good agreement with the experimental one [120]. See also Refs. [25,59,86,87].

1.3. Coordination chemistry related to hydroformylation

Equilibrated concentrations of $Co_2(CO)_8$ and $HCo(CO)_4$, obtained by the reaction of $Co_2(CO)_8$ with H_2 at a high partial pressure of dihydrogen and low partial pressure of carbon monoxide — a reagent for the stoichiometric hydroformylation reaction was studied under vacuum conditions by IR spectroscopy. It was found that upon consecutive evacuations of such reagent solutions for short periods, the formation of $HCo_3(CO)_9$ was observed [121]. Results of kinetics and thermochemistry of the oxidative addition of H_2 to the $Cr(CO)_3C_5Me_5$ radical served as a model for constructing a similar reaction profile for the reaction of $Co_2(CO)_8$ and H_2 to form $HCo(CO)_4$ [122].

The preparation and X-ray structure of $(p\text{-}{}^tBuC_6H_4CH_2)Co(CO)_3PPh_3$ and $p\text{-}ClC_6H_4CH_2C(O)]Co(CO)_3PPh_3$ has been published. These complexes are believed to be suitable model compounds for studying the stereochemistry of the alkyl–acyl equilibrium [123].

The formation of alkyne-rhodium complexes in the reaction of monosubstituted and disubstituted alkynes with tetrarhodium dodecacarbonyl under CO and CO/H_2 mixtures has been studied by in situ IR spectroscopy. $Rh_2(CO)_6\{\mu\text{-}\eta^1\text{-}(CO\text{-}R^1C_2R^2)\}$ and $Rh_2(CO)_6\{\mu\text{-}\eta^{2-}(R^1C_2R^2)\}$-type complexes were found which are stable under carbon monoxide even in the presence of molecular hydrogen. This stability under syn-gas is believed to be the reason that trace quantities of alkynes are able to poison the catalytic alkene hydroformylation reaction [124]. The reaction of hydridotetracarbonylcobalt with phenylacetylene was studied. Under an atmosphere of carbon monoxide, excess hydridotetracarbonylcobalt gives ethylbenzene and 2-phenylpropanal. When phenylacetylene is in large excess, neither ethylbenzene, 2-phenylpropanal, nor styrene is formed in more than a trace quantity. Instead a complex is formed whose spectral properties suggest that it is an alkenyl- or acylcobalt carbonyl containing a 1-phenylethenyl group [125].

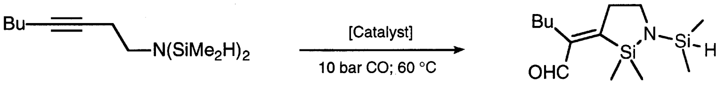
Toroid NMR probes have been employed to examine phosphine-substituted and unsubstituted cobalt carbonyl hydroformylation catalysts under catalytic and non-catalytic conditions in a variety of solvents. The high-pressure high-temperature probes allowed the observation of precatalytic equilibria under high carbon monoxide pressures in the presence and absence of dihydrogen and/or free phosphine [126].

In an attempt to understand the enhancement in catalytic activity for rhodium/iodide catalyzed methanol carbonylation utilizing the mixed P,S-donor ligand, $Ph_2PCH_2P(S)Ph_2$, the kinetics of the oxidative addition of methyl iodide to $Rh(CO)I(Ph_2PCH_2P(S)Ph_2)$ or $Rh(CO)I(Ph_2PCH_2CH_2PPh_2)$ and the subsequent CO insertion step have been investigated. It was found that while the $Ph_2PCH_2P(S)Ph_2$ ligand gives the expected fast oxidative addition, it also promotes the subsequent CO insertion step by a factor of ca. 3000 compared with $Ph_2PCH_2CH_2PPh_2$ [127]. See also Refs. [17,19,22].

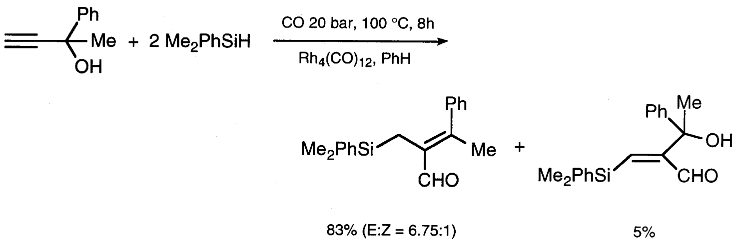
2. Hydroformylation-related reactions of CO

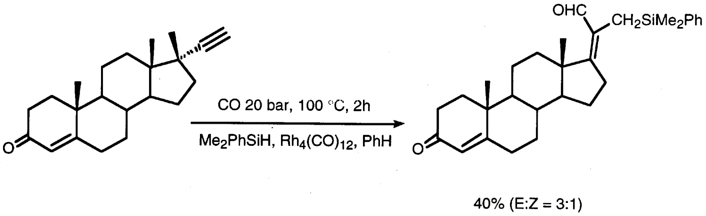
2.1. Silylformylation

The reaction of 1-bis(dimethylsilylamino)-3-octyne in the presence of $(^tBuNC)_4RhCo(CO)_4$, $Rh_2Co_2(CO)_{12}$, or Rh(acac)(CO_2 as a catalyst precursor in toluene gives at 60°C and 10 bar CO pressure 2-silyl-5-*exo*-(1-formylpentyl-1-ene)-2-aza-1-silacyclopentane as the single product in high yield by intramolecular silylformylation [128]. For example:



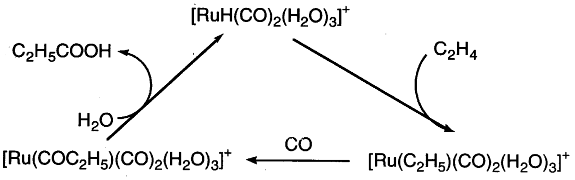
2-(Dimethylphenylsilylmethyl)-2-alkenals were prepared in a one-pot transformation of propargyl-type alcohol derivatives under silylformylation conditions [129]. For example:





2.2. Hydrocarboxylation, alkoxycarbonylation, thioformylation, and amidocarbonylation

Ethene hydrocarboxylation to propionic acid has been achieved at 140°C, P(CO) = 4 bar, $P(C_2H_4) = 30$ bar in aqueous solution in the presence of $CF_3SO_3H = 0.1$ M using 0.01 M $[Ru(COC_2H_5)(CO)_2(H_2O)_3]^+$ as the catalyst. A turnover frequency of 15.4 mol of propionic acid (mol of Ru)$^{-1}$ h^{-1} was observed. The proposed catalytic cycle involves the corresponding hydrido-, ethyl- and propionyl-complex [130].



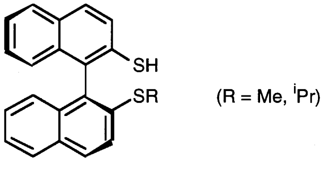
The effect of pyridine on the rate of cobalt-catalyzed olefin hydrocarboxylation has been discussed [131]. The effect of water, cobalt, and olefin concentration, partial pressure of carbon monoxide, and the pyridine:cobalt ratio in the catalyst composition on the rate of cyclohexene hydrocarboxylation was studied [132]. The role of the metal components in alkoxycarbonylation of pent-3-ene nitrile with homogeneous cobalt–ruthenium catalysts has been investigated. It was found that the addition of $Ru(acac)_3$ or $Ru_3(CO)_{12}$ to cobalt catalysts increases both activity and selectivity in the production of cyano esters [133]. The effect of cobalt(II) chloride in the $PdCl_2(PPh_3)_2$-catalyzed olefin hydrocarboxylation was studied [134].

Low symmetry palladium(II) complexes with *N*,*S*-aminothiolato ligand and PPh_3 were found to be effective catalysts for the hydrocarboxylation of styrene with 98% selectivity towards 2-phenylpropionic acid [135]. The zerovalent palladium complex $L_2Pd(dba)$ (L_2 = 1,2-bis(di-*tert*-butylphosphinomethyl)benzene, dba = *trans*,*trans*-dibenzylideneacetone) was found to be an active and selective catalyst for the production of ethyl propanoate from ethene, carbon monoxide and methanol. Thus, at 80°C and 10 bar combined pressure of ethene and CO in the presence of methane sulfonic acid and methanol, 50 000 mol methyl propanoate is produced per mol of catalyst per hour with a selectivity of 99.98% [136].

Water-soluble palladium complexes of the sodium salt of trisulfonated triphenylphosphine were found to catalyze the aqueous biphasic hydrocarboxylation of propene, 1-octene, isobutene, and cyclopentene. At 130°C and 50 bar pressure 2830 h^{-1} turnover frequency was observed in the case of the formation of butyric acid (*n*:*iso* = 58:42) [137]. The key intermediates of the palladium/TPPTS-catalyzed aqueous phase ethene hydrocarboxylation have been investigated by their NMR spectra. Kinetic investigations have shown that the conversion of the palladium-propionyl complex with water leading to the product propionic acid and regenerating the palladium-hydride complex is the rate-determining step of the catalytic cycle [138]. Biphasic hydrocarboxylation of various styrene derivatives was achieved at 100°C and 40 bar carbon monoxide pressure in high yields and selectivities in biphasic medium by using water-stable palladium/triphenylphosphine trisulfonate catalyst [139]. The addition of an alkali metal halide (such as lithium chloride) or polyvinylalcohol was found to prevent decay and to maintain high activities of the water-soluble hydrocarboxylation catalyst derived from $PdCl_2$ and the sulfonated phosphine trisodium tris(*m*-sulfonatophenyl)phosphine in the conversion of propene into a mixture of 2-methylpropanoic acid and butanoic acid (toluene–water, 100–120°C, P(CO) = 40 bar) [140].

The synthesis of 2-(4-isobutylphenyl)propionic acid (Ibuprofen) was studied by hydrocarboxylation of 1-(4-isobutylphenyl)ethanol with CO and water in the presence of the $PdCl_2$–PPh_3–HCl catalyst system. An almost regiospecific synthesis (98% selectivity) was achieved at 125°C and 50 bar CO pressure [141]. Anchoring the catalyst on montmorillonite showed an even better selectivity to Ibuprofen than the homogeneous catalyst [142].

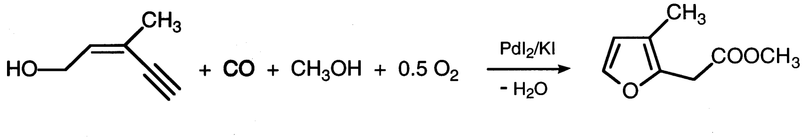
In alkoxycarbonylation of 1-arylethanols and styrenes catalyzed by $PdCl_2(PPh_3)_2$ and an acid, the regioselectivity was found to be very sensitive to the nature of the counter anion of the acid. Thus, chloride anion favors branched products, while tetrafluoroborate and sulfonate anions favor linear products at 90°C and 50 bar carbon monoxide pressure in methanol–CH_2Cl_2 solution [143]. High-branched selectivity (up to 97%) was observed in the palladium-catalyzed alkoxycarbonylation of styrene in the presence of thiol–thioether atropisomeric ligands **48** and PPh_3 at 100°C, 30 bar carbon monoxide in oxalic acid-containing dimethoxyethane [144].



48

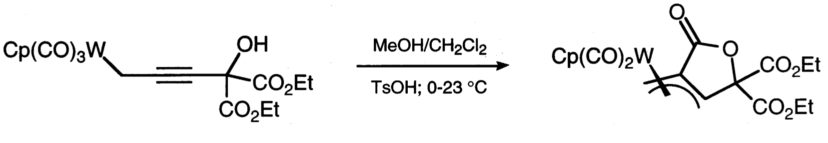
High-molecular weight (98 000–200 000) carboxylated polybutadienes with 0.5–10 mol% COOH-content were synthesized by hydrocarboxylation of polybutadienes at 140–150°C using $PdCl_2(PPh_3)_2$ and $SnCl_2{\cdot}2H_2O$ as the catalyst [145]. Catalytic pathways of styrene and α-methyl styrene hydroalkoxycarbonylation in the presence of $PdCl_2(PPh_3)_2$ and $PdCl_2(PPh_3)_2/SnCl_2$ catalyst precursors have been investigated by deuterium-labeling with EtOD. Based on mass spectral analysis and NMR-identification of the deuterated reaction products the 'hydrido'-route (olefin insertion into the Pd–H bond followed by CO insertion and product formation reaction with the alcohol) was deduced [146,147].

The alkoxycarbonyl complex $Pd(Ph_2Ppy)_2(CO_2CH_3)(CO_2CF_3)$ ($Ph_2Ppy = 2$-pyridyl-diphenylphosphine) was found to be a catalyst in alkoxycarbonylation of phenylacetylene at r.t. and 30 bar CO pressure [148]. A variety of (*Z*)-2-en-4-yn-1-ols have been carbonylated under oxidative conditions to obtain substituted furan-2-acetic esters in good yields. The cyclization–alkoxycarbonylation process occurs in alcoholic media at 50–70°C under 100 bar pressure of a 9:1 mixture of CO and air in the presence of KI and catalytic amounts of PdI_2 [149]. For example:



73% isolated yield

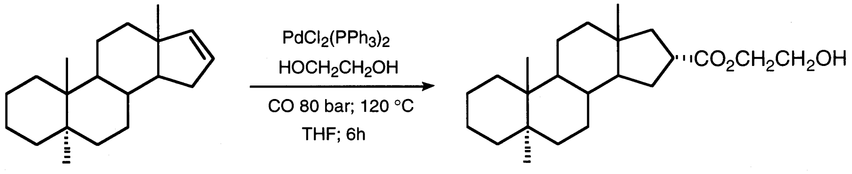
Intramolecular alkoxycarbonylation of propargyltungsten complexes has been applied among the key steps in the syntheses of natural bislactones [150]. For example:



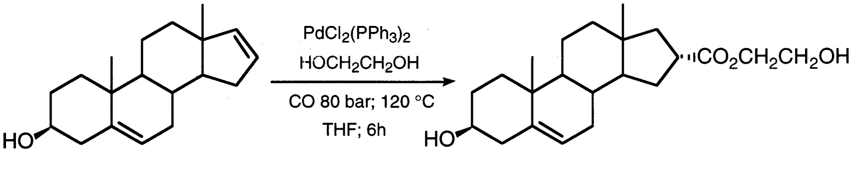
65% isolated yield

Stereoselective synthesis of substituted tetrahydropyranes has been achieved by intramolecular palladium-catalyzed alkoxycarbonylation of 6-hydroxy-1-octenes [151].

Δ^{16}-Steroids were found to give the corresponding 16-α-ester derivative in high yield by palladium-catalyzed alkoxycarbonylation [152]. For example:



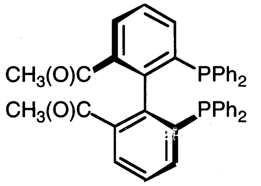
81%



91%

The cyclocarbonylation of isopulegol catalyzed by palladium(II) complexes containing no chiral ligands was found to produce the two compounds (1*R*,5*R* or 5*S*,6*S*,9*R*)-5,9-dimethyl-2-oxabicyclo[4.4.0]decane-3-one with a diastereomeric excess up to 60% [153].

Cationic palladium(II) complexes of the type [Pd(L–L)(solvent$_2$)]X$_2$ (where L–L is a chelate ligand with C_2 symmetry such as **49** and X is an anion with low coordination properties such as trifluoroacetate) were found to catalyze the enantioselective bis-alkoxycarbonylation of 1-olefins to substituted succinates at 50°C and 350 bar CO pressure in the presence of 1,4-benzoquinone in methanol solution. In the best case, 93% ee of (*S*)-**50** was obtained from styrene [154].



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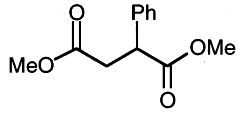

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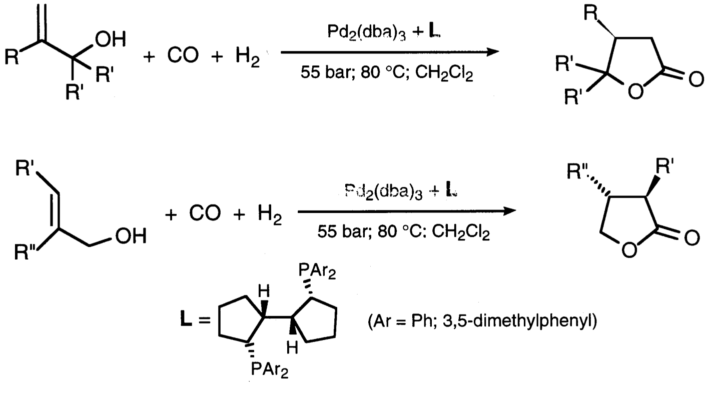
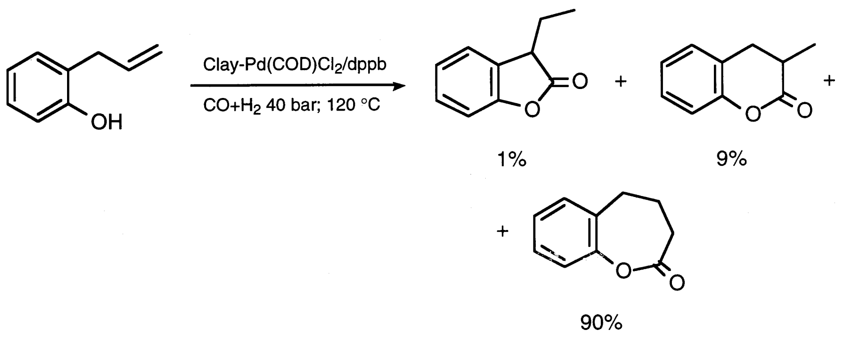
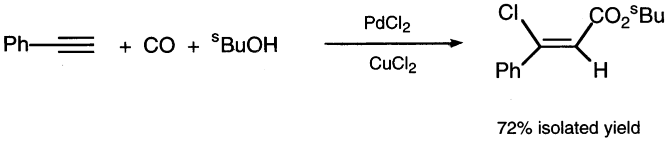
Highly enantioselective cyclocarbonylation of allylic alcohols (up to 98% ee) have been achieved in palladium-catalyzed reactions in the presence of chiral phosphines [155].



Palladium-clays, prepared using montmorillonite and either dichloro(1,5-cyclooctadiene)palladium(II) or dichlorobis(benzonitrile)palladium(II), were found to be effective catalysts for the carbonylation of 2-allylphenols, affording seven-membered ring lactones as the principal products [156]. For example:

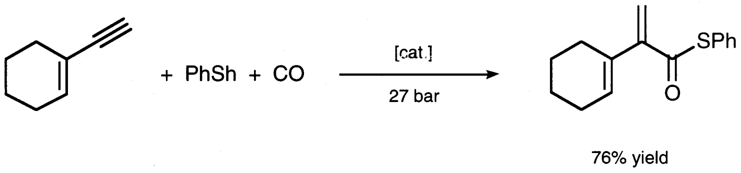


Isolated yields of (*Z*)-3-chloroacrylate esters ranging from 30% to 72% were obtained in the alkoxycarbonylation of terminal acetylenes in the presence of catalytic amounts of $PdCl_2$ and 3 equivalents of cupric chloride at r.t. and 1 bar carbon monoxide pressure [157]. For example:



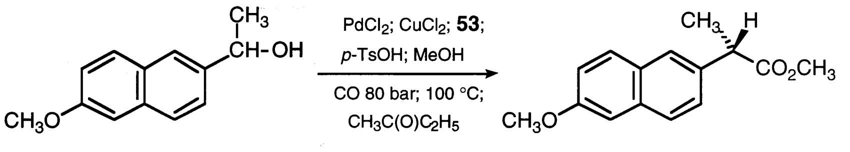
Propionamide and propionitrile were formed by passing the mixture of ethene, carbon monoxide, and ammonia under atmospheric pressure at 200°C over a silica- or zeolite-supported ruthenium amine complex $[Ru(NH_3)_6]^{3+}$ catalyst. The rhodium amine complex $[Rh(NH_3)_6]^{3+}$ also promoted the reaction but the catalytic activity was low. It was inferred that propionamide is formed primarily and is dehydrated successively on the support [158].

The reaction of 1,3-conjugated enynes bearing a terminal triple bond with thiols and carbon monoxide in the presence of 3 mol% $Pd(OAc)_2$ and 6 mol% 1,3-bis-(diphenylphosphino)propane in THF at 110°C was found to give 2-phenylthiocarbonyl-1,3-dienes in moderate to good yields [159]. For example:

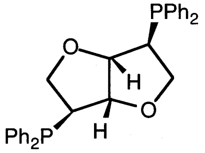


High initial rates were observed in the cobalt-catalyzed methanol carbonylation if $Cp^*Co(CO)_2$ was used in the presence of PEt_3 and MeI at 120°C and 100 bar carbon monoxide. The observed activities of the cobalt catalysts were found to be comparable with those of their rhodium-based analogs [160]. The mixed-metal carbonyl cluster anion $[Os_3Ir(CO)_{13}]^-$ was found to be an active catalyst for methanol carbonylation in the presence of CH_3I as co-catalyst. Turnover numbers up to 1800 were observed at 140°C and 30 bar within 14 h [161]. Results of in situ cylindrical internal reflectance FTIR investigation of the nickel-catalyzed carbonylation of methanol at 160°C in the presence of CH_3I or LiI led to the suggestion of $Ni(PPh_3)_2$ as the repeating active species in the catalytic cycle [162]. A reversible slow oxidative addition of CH_3I to $Ni(PPh_3)_2$ and much faster subsequent steps were proposed for the mechanism [163]. In the presence of a large excess of iodide, palladium and platinum salts were found to catalyze the carbonylation of methyl iodide in methanol to methyl acetate at 5 bar CO and 140°C. The highest turnover, ca. 110/16 h were found using $[PdCl_2(PPh_3)_2]$ and Bu_4NI as additive. A possible catalytic cycle for methanol carbonylation based on participation of Pd(II) and Pd(IV) complexes was suggested [164].

Asymmetric carbonylation of **51**–**52** [(*S*)-Naproxen] has been achieved in a $PdCl_2$–$CuCl_2$–DDPPI (DDPPI = 1,4:3,6-dianhydro-2,4-dideoxy-2,5-bis(diphenylphosphino)-L-iditol (**53**)) catalytic system with chemical yield of 90% and an optical yield of 81% ee [165].



51 **52**



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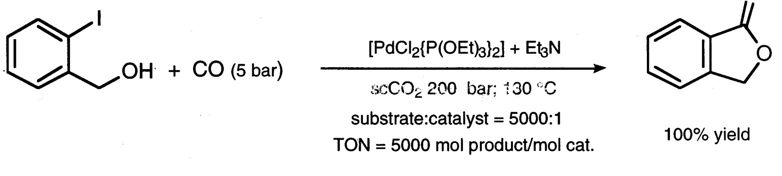
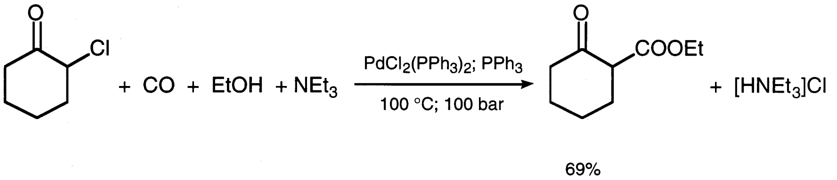
A rhodium complex supported on polyvinylpyrrolidone was found to catalyze the carbonylation of methanol to methyl acetate and acetic acid in supercritical carbon dioxide at rates up to ca. 50% of those in liquid solution but with minimal catalyst leaching [166].

Rhodium triethylphosphine complexes were found to catalyze the dicarbonylation of diiodomethane in alcoholic solvents to malonate esters. Intermediates postulated in the catalytic cycle, or close analogous of these, were isolated and characterized [167].

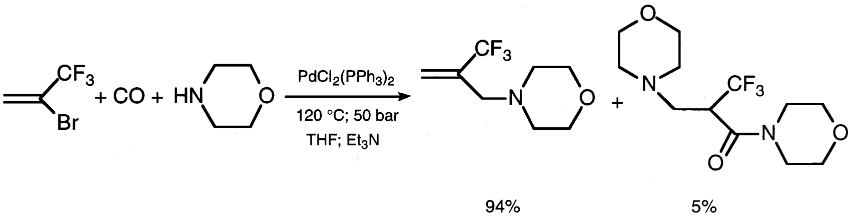
Carbonylation of 2-iodobenzyl alcohol in supercritical carbon dioxide in the presence of trialkyl or triaryl phosphite complexes of palladium give selectively the corresponding phthalide [168].



The carbonylation of 2-chlorocyclohexylketone in the presence of NEt_3 and $PdCl_2(PPh_3)_2$–PPh_3 as the catalyst precursors was found to occur with good yields at 60–100°C and 50–100 bar CO pressure [169]. For example:



Alkoxycarbonylation of 2-bromo-3,3,3-trifluoropropene at 100°C and P(CO) = 50 bar in the presence of $PdCl_2(PPh_3)_2$ resulted in high substrate conversion, but the yield of 2-(trifluoromethyl)acrylic acid ester was low (16–36%) because the unsaturated ester reacts further adding a molecule of alcohol to the carbon–carbon double bond. In the presence of secondary amines the corresponding unsaturated amides are produced in high yields. For example:

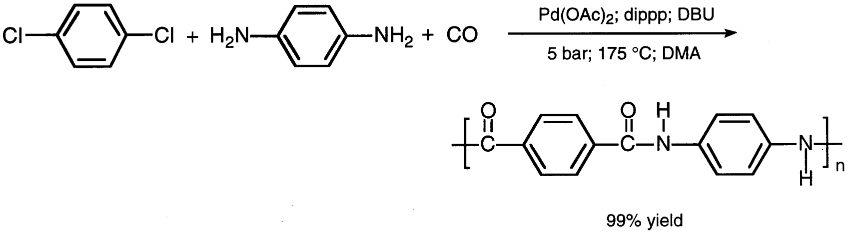


The methyl ester of 2-trifluoromethylacrylic acid was obtained in good yield by hydromethoxycarbonylation of 3,3,3-trifluoropropyne using the catalytic system: $Pd(OCOCH_3)_2$/2-pyridyldiphenylphosphine/CH_3SO_3H. The regioselectivity of the reaction can be controlled by suitable choice of the solvent [170].

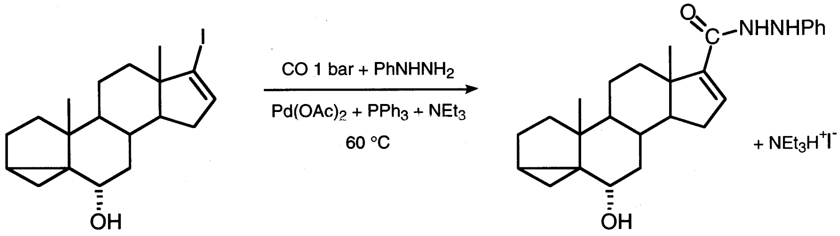
Selective catalytic alkoxycarbonylation or amidocarbonylation of 6,17-diiodo-4-aza-androsta-5,16-dien-3-one in the 17 position was found using methanol or piperidine, respectively, in the presence of $Pd(OAc)_2/2PPh_3/60Et_3N$ in DMF under carbon monoxide at 60°C [171].

Chloroacyl halides were obtained under mild conditions (100°C, 4h, P(CO) = 24 bar, P(HCl) = 9 bar by catalytic carbonylation of allylic halides or ethylene and allyl chloride mixtures in the presence of $PdCl_2$ in halogenated hydrocarbons as the solvent [172].

Aromatic polyamides (aramids) were obtained in a novel catalytic procedure from dichloarenes, diaminoarenes and carbon monoxide. Suitable catalysts for the reaction are palladium complexes containing bulky ligands, such as dippp (dippp = 1,3-diisopropylphosphino)propane) [173]. For example:

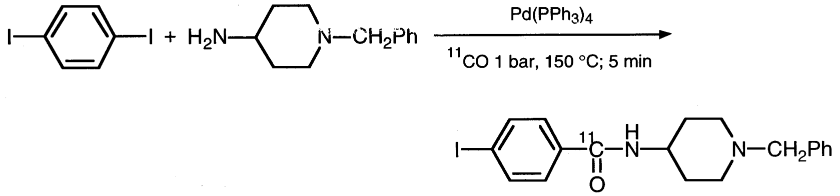


Various N-substituted steroidal hydrazides were prepared in high yields from 17-iodo(bromo)androst-16-enes by homogeneous palladium-catalyzed hydrazinocarbonylation [174]. For example:



>98% conversion, 94% isolated yield

Biologically active ^{11}C-labeled amides have been prepared from aryl halides and [^{11}C]carbon monoxide in palladium-mediated reactions [175]. For example:



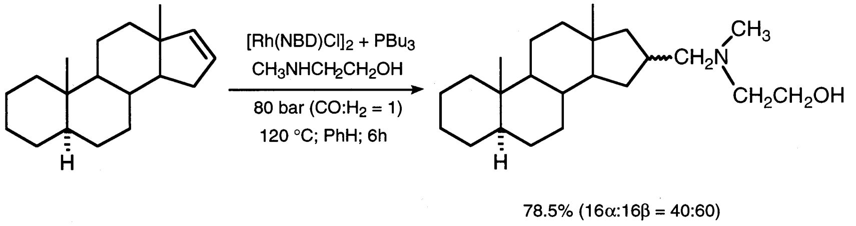
See also Refs. [117–119].

2.3. Hydroaminomethylation

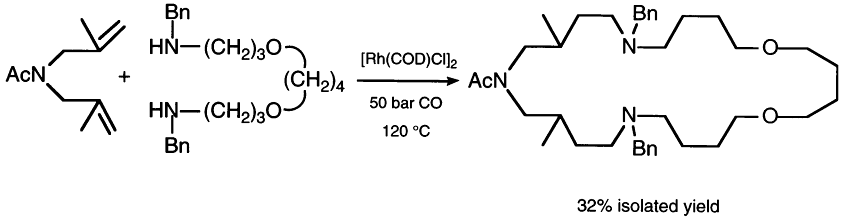
In an effect to obtain high *n*:*iso* ratios in hydroaminomethylation of propene in the presence of piperidine various ruthenium compounds were tested at 120°C and 45 bar CO:H$_2$ = 1:2. The best result using $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ as the catalyst precursor in acetonitrile is 99% selectivity and 95% linearity (*n*/*iso* = 18) for 59% conversion [176].

The preparation of aliphatic amines from aliphatic 1-olefins and alicyclic diamines from dicyclopentadiene by hydroaminomethylation employing a rhodium–ruthenium catalyst has been investigated. Up to 97% selectivity towards the amines at conversions of up to 98% has been observed in the case of aliphatic monoolefins, such as 1-dodecene at 150°C and 150 bar CO:H$_2$ = 1:1 pressure [177].

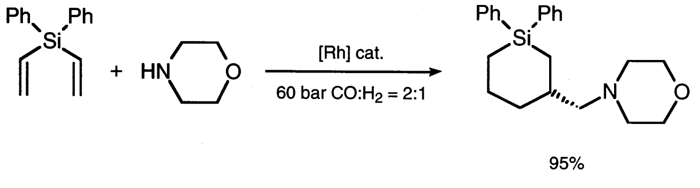
New 16-aminomethyl derivatives of steroids were prepared from Δ^{16} steroids by rhodium-catalyzed one-pot hydroaminomethylation in moderate to good yields [178]. For example:



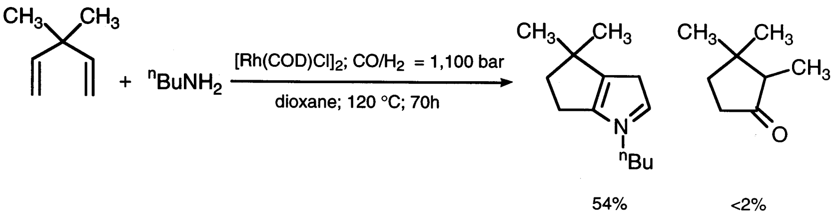
The rhodium-catalyzed one-pot hydroaminomethylation of dienes in the presence of α,ω-diamines has been used for 13–36 membered macroheterocyclic ring synthesis [179]. For example:

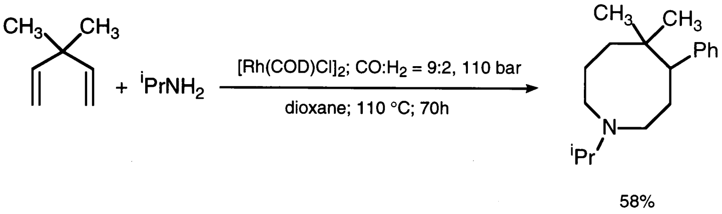


Pharmacologically-active derivatives of phenothiazine, iminodibenzyl, carbazole and pyrazole have been prepared with high yields and chemoselectivity by the reaction of the corresponding *N*-allylic or *N*-methallylic compounds, primary or secondary amines, carbon monoxide and dihydrogen in the presence of $[Rh(COD)Cl]_2$ as catalyst precursor via a one-pot hydroformylation–amine condensation–reduction sequence [180]. Divinylsilanes and secondary amines in the presence of $Rh(acac)(CO)_2$ and triphenylphosphine gave in a selective one-pot tandem hydroformylation–condensation sequence aminomethyl-substituted silacyclohexane derivatives in up to quantitative yields [181]. For example:

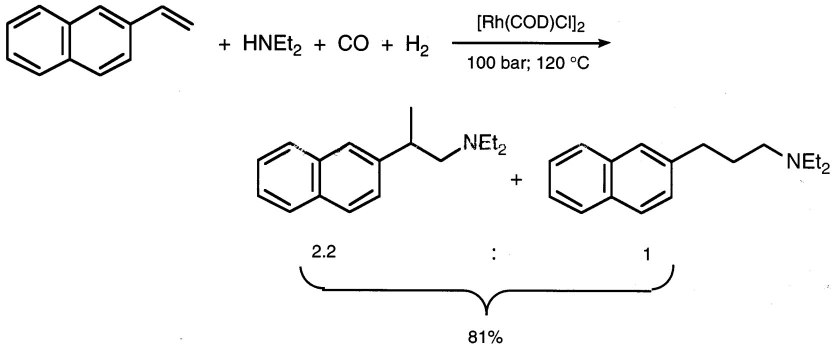


Pyrroles and eight-membered heterocycles were prepared from 1,4-dienes via rhodium-catalyzed ring-closing hydroaminomethylation. The selectivity of the reaction was found to be controlled by the substitution pattern of the diolefin [182]. For example:

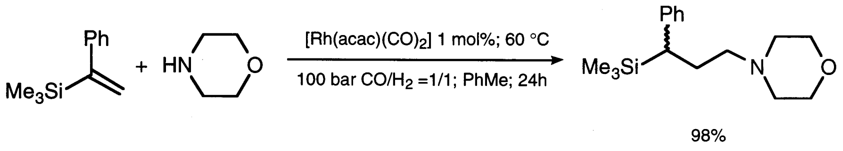


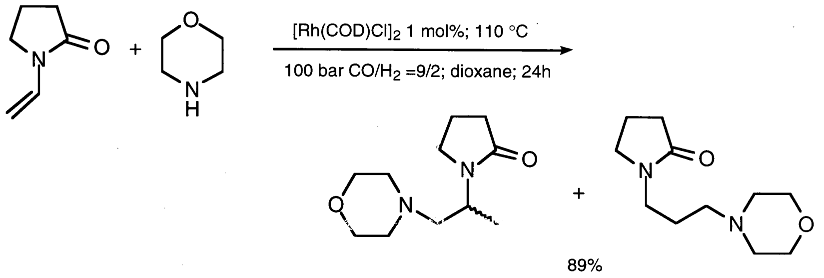


Carbonylative hydroaminomethylation of 2-vinylnaphthalene with primary or secondary amines, 50 bar CO and 50 bar H_2 in the presence of $[Rh(COD)Cl]_2$ as the catalyst precursor at 120°C gave the corresponding secondary or tertiary amines, respectively in 81–92% yields [183]. For example:

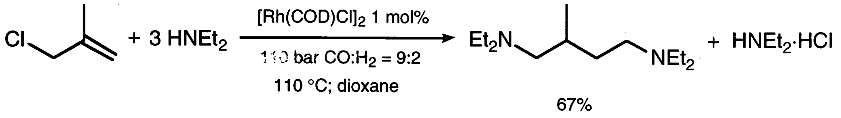


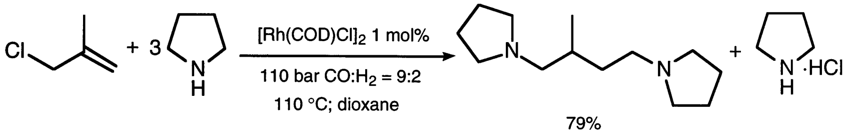
The combination of hydroformylation and subsequent reductive amination as a one-pot hydroaminomethylation procedure for vinylsilanes or enamines results in β- and γ-aminofunctionalized silanes or 1,2- and 1,3-diamines, respectively, in good to excellent yields [184]. For example:



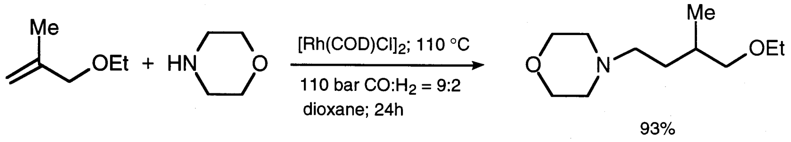


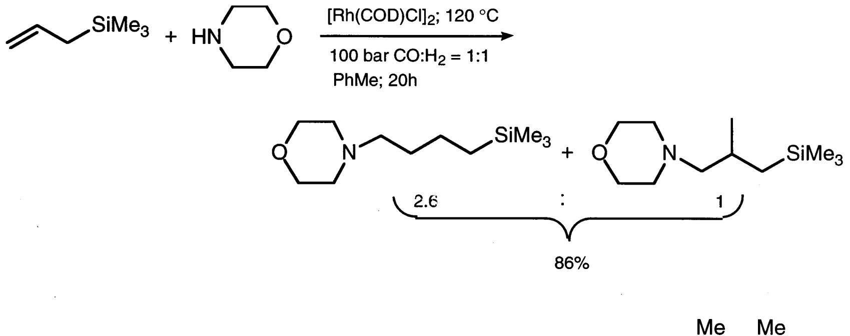
From methallyl chloride and 3 equivalents of secondary amines in a one-pot multistep reaction sequence under rhodium-catalyzed hydroaminomethylation conditions, 1,4-diamines are formed in 67–79% yields [185]. For example:

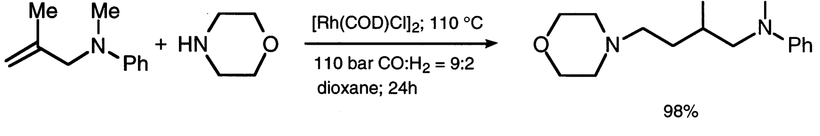




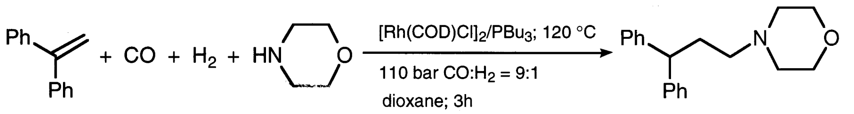
The rhodium(I)-catalyzed one-pot hydroaminomethylation was found to be an efficient method to generate γ-amino- and δ-amino-functionalized ethers, amines, and silanes in high yields [186]. For example:



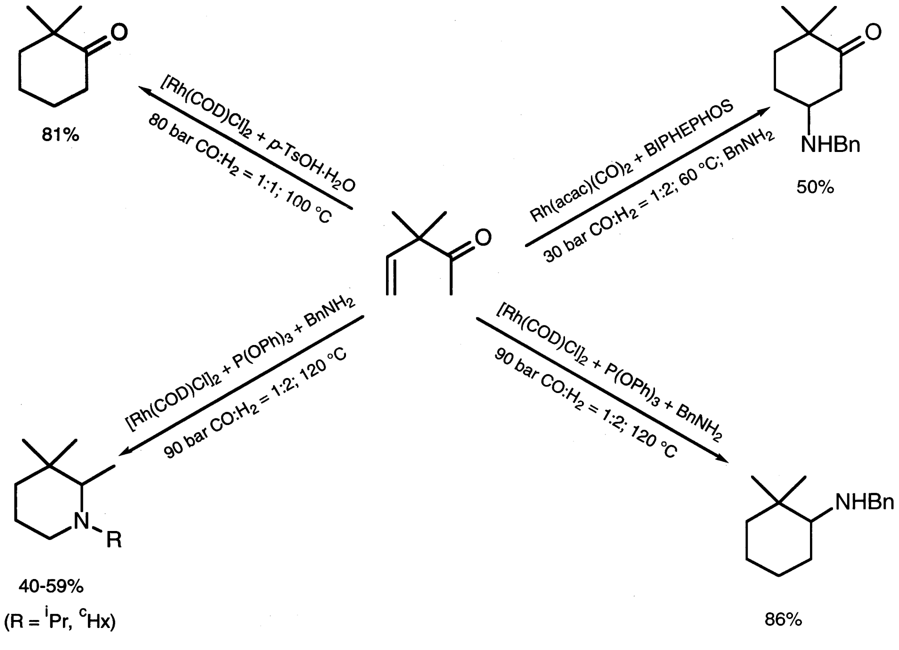




Pharmacologically-active secondary and tertiary 1-(3,3-diarylpropyl)amines were prepared in 68–76% yields and high chemoselectivity by a one-pot synthesis from 1,1-diarylethenes, primary or secondary amines, CO and H_2 in the presence of $[Rh(COD)Cl]_2/PBu_3$ as the catalyst precursors via a hydroformylation–amine condensation–reduction sequence. With this catalyst the enhanced tendency of 1,1-diaryl ethenes towards hydrogenation is effectively suppressed by the PBu_3-catalyst component [187]. For example:



Rhodium(I)-complex catalyzed tandem hydroformylation/aldol reactions of a β,γ-unsaturated ketone or its silyl enol ethers in a one-pot procedure have been described to give varying cyclization products depending on the reaction conditions [188]. For example:

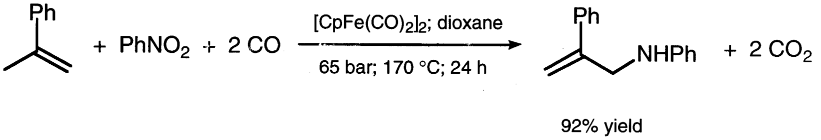


A highly selective hydroaminomethylation of olefins (propene, 1-butene and 1-pentene) with ammonia to form linear primary and secondary aliphatic amines was achieved by using a new rhodium–iridium–BINAS catalyst system in a two-phase methyl *tert*-butyl ether/water media. Amine yields up to 95% have been observed [189]. See also Refs. [27,38].

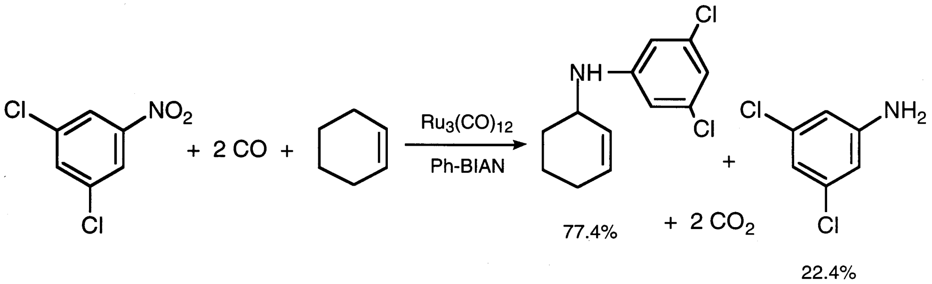
2.4. Water–gas shift reaction and reduction with CO or $CO + H_2O$

Revision of the homogeneously pentacarbonyliron-catalyzed water–gas shift reaction in the gas phase was performed by quantum chemical calculations using gradient-corrected density functional theory and ab initio methods. The classically assumed reaction path was scrutinized step by step, and enlarged with novel mechanistic proposals [189].

Reactions of olefins with nitroarenes catalyzed by 5 mol% $[CpFe(CO)_2]_2$ in dioxane at 150–180°C under 50–75 bar carbon monoxide pressure give the corresponding allylic aminated products [191]. For example:



Reduction of aromatic nitro compounds, $Ar'NO_2$, by carbon monoxide was found to be catalyzed by $Ru_3(CO)_{12}$ in the presence of Ar-BIAN (Ar-BIAN = bis(arylimino)-acenaphthene, aryl = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4), in commercial cyclohexene as solvent at 160°C and 40 bar. The main product of the reaction is the corresponding allylamine derivatives. Byproducts of the reaction are the corresponding anilines [192]. For example:



The mechanism of the $Ru_3(CO)_{12}$/tetraalkylammonium halide-catalyzed carbonylation of nitroarenes to carbamates has been investigated. It was found that the reaction proceeds through the intermediate formation of aniline and that the active ruthenium species is mononuclear and not a cluster [193].

A series of ruthenium mono(bipyridine) carbonyl complexes $Ru(L)(CO)_2X_2$ (L = 2,2′-bipyridine or methyl-substituted 2,2′-bipyridine; X = Cl, H, SCN, $C(O)OCH_3$) were studied as potential catalysts in the water–gas shift reaction [194]. Silica-supported ruthenium mono(bipyridine) carbonylchloride $Ru(bpy)(CO)_2Cl_2/SiO_2$ was found to show high activity in water–gas shift catalysis after treatment with sodium hydroxide. Turnover frequencies as high as 14 500 mol CO_2 (mol Ru)$^{-1}$ day^{-1} at 150°C were observed [195].

The reaction product of the complexes $Ru_3(CO)_{12}$, $Ru_6C(CO)_{17}$, $H_4Ru_4(CO)_{12}$, and $H_2Os_3(CO)_{10}$ with the phosphine $P(m\text{-}C_6H_4SO_3Na)_3$ were found to be effective water-soluble cluster catalyst precursors in the water–gas shift reaction [196].

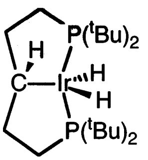
Rhodium-catalyzed carbonylation of 2-phenylethynylbenzaldehyde or 2-phenylethynylbenzoate under water–gas shift reaction conditions ($Rh_6(CO)_{16}$, Et_3N, H_2O, $CHCl_3$, 100 bar CO, 80–180°C) was found to result in the formation of indeno[1,2-*b*]furan or indeno[1,2-*c*]isocumarin, respectively [197].

The reductive carbonylation of nitroaromatics under 80 bar partial pressure of carbon monoxide at 140°C was investigated using $RhA(CO)_2$ (HA = anthranilic acid) as the catalyst precursor. The maximum yield and selectivity of the carbamate product were achieved by using NaOMe and MeOH as cocatalyst and cosolvent, respectively [198].

The water–gas shift reaction catalyzed by *cis*-$[Rh(CO)_2(\text{amine})_2]PF_6$ (amine = 4-picoline, 3-picoline, 2-picoline, pyridine, or 2,6-lutidine) heterogenized on poly(4-vinylpyridine) an aqueous 2-ethoxyethanol was investigated. The rhodium complex containing 4-picoline ligands was found to be the most active displaying turnover frequencies for dihydrogen production of 8.9 mol H_2 (mol Rh)$^{-1}$ day^{-1} for 9.4×10^{-5} mol *cis*-$[Rh(CO)_2(\text{4-picoline})_2]PF_6$/1.00 g poly(4-vinylpyridine), at 100°C and P(CO) = 0.9 bar [199]. Similar results have been obtained using the corresponding rhodium–COD–amine complexes in the preparation of the catalyst [200].

Homogeneous catalysts prepared from rhodium trichloride in aqueous aromatic amines such as 4-picoline, have been found to reduce carbon–chlorine bonds under mild water–gas shift conditions (100°C and 1 bar CO) [201].

Intermediate metallo-formate complex has been detected by NMR spectroscopy in the reverse water–gas shift reaction ($CO_2 + H_2 = CO + H_2O$) modeled by the interaction of carbon monoxide with **54** [202].



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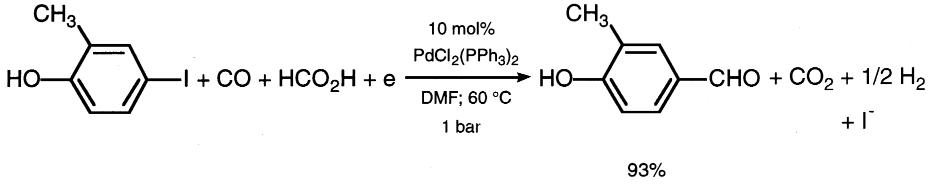
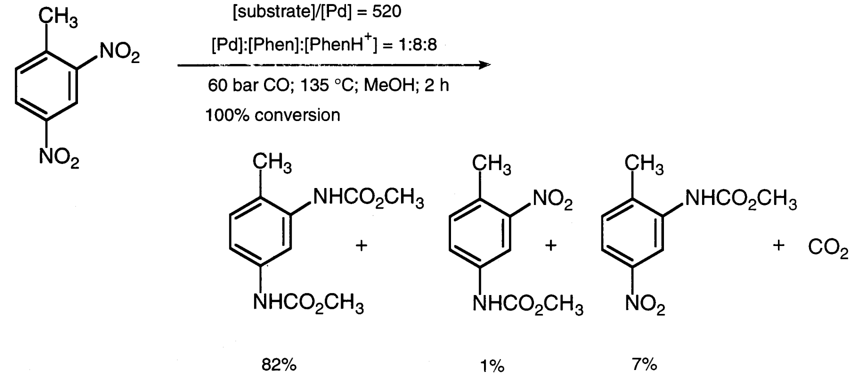
The palladium-catalyzed electrocarbonylation of aryl halides performed in the presence of formic acid under 1 atm of carbon monoxide was found to afford aromatic aldehydes in good to high yields [203]. For example:



Reductive carbonylation of 2,4-dinitrotoluene to 2,4-toluendiurethane with palladium(1,10-phenanthroline)$_2$(hexafluorophosphate)$_2$ as catalyst and 1,10-phenanthrolinium hexafluorophosphate as cocatalyst has been achieved with 60 bar CO pressure at 115–160°C in dry methanol solution [204].



See also Refs. [117,118].

2.5. Reduction of CO and CO$_2$

Water-soluble ruthenium(II)– and rhodium(I)–phosphine complexes were found to catalyze the hydrogenation of aqueous hydrogen carbonate to formate under mild conditions. Thus, 2.0–2.5 mM solutions of [RhCl(tppms)$_3$] (tppms = 3-sulfonatophenyldiphenylphosphine) in 1.0 M aqueous NaHCO$_3$ under 5 bar CO$_2$ and 35 bar H$_2$ at 24°C in the presence of free tppms (total P:Rh = 7:1), produced in 2 h, 524 mol formate (mol Rh)$^{-1}$ [205].

A mesoporous ruthenium silica hybrid aerogel containing well-dispersed bidentate RuCl$_2$[Ph$_2$P(CH$_2$)$_3$PPh$_2$]$_2$ complexes was found to afford turnover frequencies up to 18 400 h^{-1} and 100% selectivity for the formation of *N*,*N*-diethylformamide from CO$_2$, H$_2$ and diethylamine at 110°C and 180 bar total pressure [206].

Carbon monoxide hydrogenation in the liquid phase was carried out at 100 and 150°C with an initial pressure of 50 bar using a catalyst composed of a metal (Cr, Mo, W, or Ni) carbonyl and potassium methoxide. Among the metal carbonyls tested, nickel tetracarbonyl showed a peculiarly high production of methanol. In 1 h at 100°C using 10 mmol Ni(CO)$_4$, 40 mmol CH$_3$OK in triglyme, 173.3 mmol methanol is formed [207].

Methanol was prepared from syn-gas at 100°C and 18 bar (CO:H$_2$ = 2:1) using the homogeneous Ni(CO)$_4$/KOMe catalytic system. The effect of additives on the catalytic activity decreased in the order: DMSO > 2-hydroxybenzothiazole > triethylamine ~ pyridine > 2-amino-4-methylpyridine ≫ CH$_3$CN [208].

The complex Ni(cyclam)$^+$ was found to mediate the two-electron reduction of carbon monoxide and protons in homogeneous aqueous solution. The reduction kinetics were studied by pulse radiolysis. Product analysis studies following continuous γ-radiolysis demonstrated that carbon monoxide and/or dihydrogen were formed with near quantitative yield [209]. See also Ref. [77].

3. Reviews

1. Homogeneous catalysis in supercritical fluids. A review with 187 references among others about hydroformylation in supercritical fluids [210].
2. Homogeneous catalysis — towards greener chemistry (20 references) [211].
3. Fluorous phase separation techniques in catalysis. A review with 39 references about the application and potential of fluorous solvents in rhodium-catalyzed olefin hydroformylation [212].
4. The aminophosphine–phosphinite and related ligands: synthesis, coordination chemistry and enantioselective catalysis. A review with 107 references among others about the application of aminophosphine–phosphinite ligands in rhodium- and platinum-catalyzed asymmetric hydroformylation [213].
5. New rhodium hydroformylation catalysts. A review with 46 references about mono- and diphosphite modified rhodium catalyst in hydroformylation including asymmetric hydroformylation of styrene [214].
6. Oleochemistry. A review with 79 references about typical examples of the conversion of fatty compound by hydroformylation, hydrocarboxylation and oxidation reaction [215].
7. New opportunities in hydroformylation: selected syntheses of intermediates and fine chemicals. A review with many references on preparation of intermediates and fine chemicals by hydroformylation [216].
8. Re-immobilization techniques. A review with ca. 38 references on catalyst systems for hydroformylation processes using functionalized ligands to enable phase separation [217].
9. Polymer support effects of metal complexes for catalysis. A review with 18 references on the effects of polymer supports on the activity and selectivity of metal-complex catalysts among others for hydroformylation of olefins [218].
10. Polymer supports in synthesis. A brief review with references on rhodium(I) complexes with new and improved chiral phosphorus-based binaphthyl ligands as catalysts for asymmetric hydroformylation of styrene and vinyl acetate [219].
11. Chemistry in interphases — a new approach to organometallic syntheses and catalysis. A review about the application of polymer-bound reagents and catalysts among others in hydroformylation. 274 References [220].
12. New directions in water-soluble homogeneous catalysis. A review of the role of water-soluble ligands in the immobilization of homogeneous catalysts (40 references) [221].
13. Biphasic oxo process. The development of biphasic catalytic processes for olefin hydroformylation to aldehydes is reviewed and future developments are discussed [222].

14. Bulk and fine chemicals via aqueous biphasic catalysis. A review with 97 references on application of homogeneous aqueous biphasic catalysis among others in hydroformylation [223].
15. Environmental and safety aspects. A review with 22 references on the environmental and safety aspects of a two-phase catalytic process for hydroformylation of propylene to butyraldehyde [224].
16. Conversion of functionalized olefins. A review with 22 references on two-phase catalytic processes for hydroformylation of functionalized olefins [225].
17. Versatile inverse phase-transfer catalysts for the functionalization of substrates in aqueous-organic two-phase systems: the chemically modified β-cyclodextrins. A review with 17 references about the application of chemically modified β-cyclodextrins among others in biphasic hydroformylation and hydrocarboxylation of water insoluble olefins [226].
18. Advances in transition-metal catalyzed hydroxycarbonylation reactions in aqueous–organic two-phase systems. A review with 57 references [227].
19. New supramolecular transition metal catalysts. A review with 30 references about the application of a new type of supramolecular catalyst among others in 1-octene hydroformylation in a two-phase system in which molecular recognition, phase-transfer catalysis and transition metal catalysis are combined in a single system [228].
20. Higher olefins. A review with 48 references on a two-phase process for hydroformylation of higher olefins using rhodium phosphine complex catalysts [229].
21. Progress in the research and development of two-phase (water–organic) hydroformylation of olefins. A review with 25 references [230].
22. Catalysts derived from hydrogen absorbing intermetallics. A review with 47 references of the absorbing intermetallics as catalysts among others for carbon monoxide hydrogenation [231].
23. Syntheses of hydrocarbons from ethene-containing gases. A review with 77 references of hydrocarbon synthesis including among others the modified Fischer–Tropsch synthesis from CO, H_2, and ethene [232].
24. Homogeneous transition metal catalysis: from the water–gas shift reaction to nuclear waste vitrification. A review with 37 references about two decades of research on homogeneous catalysis at the University of Georgia [233].
25. Homogeneous catalysis with transition metal complexes. A review with 83 references among others about the current status, further developments of concepts and techniques in relation to present and potential industrial application of rhodium-catalyzed hydroformylation [234].
26. Perspectives of rhodium organometallic catalysis. Fundamental and applied aspects of hydroformylation. A review with 78 references [235].
27. Transition metal-catalyzed chemospecific reduction of aromatic nitro compounds, and hydrocarbonylation of chlorobenzenes under CO/H_2 conditions. A review with 92 references [236].
28. Tandem reaction sequences under hydroformylation conditions: new synthetic applications of transition metal catalysis. A review with 311 references about

the chemistry and examples of two or more step conversions of unsaturated compounds under hydroformylation involving initial hydrocarbonylation and additional conversions of intermediates or the aldehyde product covering the literature up to the end of 1998 [237].

29. Homogeneous catalysis with transition metal complexes containing sulfur ligands. A review with 289 references about the application of complexes containing sulfur ligands among others in carbonylation and hydroformylation [238].

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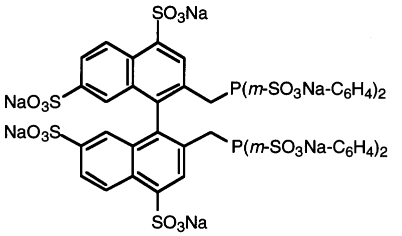
Appendix A. List of abbreviations

Ac	acetyl
Ar	aryl
acac	acetylacetonate
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
BINAPHOS	See **27**
BINAS	
BIPHEPHOS	See **18**
Bn	benzyl
bpy	2,2′-bipyridine
Bu	butyl
Bz	benzoyl
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
cyclam	1,4,8,11-tetraazacyclotetradecane
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DIPHOS	$Ph_2PCH_2CH_2PPh_2$
dippp	${}^{i}P_2PCH_2CH_2CH_2P^{i}Pr$
DMA	*N*,*N*-dimethylacetamide
DMF	*N*,*N*-dimethylformamide

DMSO	dimethylsulfoxide
dppe	$Ph_2PCH_2CH_2PPh_2$
$EDTAH_2$	ethylenediaminetetraacetic acid
ee	enantiomeric excess
Et	ethyl
^{c}Hx	cyclohexyl
IR	infrared
Me	methyl
NBD	norbornadiene
Ph	phenyl
Phen	1,10-phenanthroline
py	pyridine
sc	supercritical
THF	tetrahydrofuran
TN	turnover number (mol product/mol cat)
TOF	turnover frequency (mol product/mol cat/time)
TPPMS	sodium-*m*-(diphenylphosphino)benzene sulfonate
TPPTS	trisodium salt of the trisulfonated triphenylphosphine
Ts	*p*-toluenesulfonyl (tosyl)

Appendix B. The metals and their associated references

Metal	Refs.
Cr	[122,207]
Mo	[72,207]
W	[72,150,207]
Fe	[190,191]
Ru	[54,70,71,81,95,130,133,158,176,177,192–196,205,206]
Os	[161,196]
Co	[1–7,77–79,96,121–123,125,126,128,131–134,160]
Rh	[2,3,5,6,8–69,72,77–94,97–114,117,118,124,126–129,158,166,167,177–189,197–201,205,212–214,219,220,235]
Ir	[30,81,161,189,202]
Ni	[162,163,205,208,209]
Pd	[81,134–149,151–157,159,164,165,168–175,203,204]
Pt	[73–76,81,164,213]
Cu	[151,157,165]
Sn	[73,74,76,145–147]

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