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Application of transition metals in hydroformylation. Annual survey covering the year 1994 ★

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Contents

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1. Hydroformylation

1.1. Homogeneous systems

1.1.1. Cobalt catalysts

The hydroformylation of 1-pentene using $PhCCo_3(CO)_9$ as the catalyst precursor has been examined by cylindrical internal reflectance spectroscopy. At 130 °C, cluster fragmentation is observed, and the formation of aldehydes is shown to coincide with the fragmentation of $PhCCo_3(CO)_9$. Cylindrical internal reflectance spectral data for the $Co_2(CO)_8$-catalyzed hydroformylation of 1-pentene are also presented for comparative purposes [1]. Using $PhCCo_3(CO)_7(L\text{-}L)$ ($L\text{-}L = cis\text{-}Ph_2PCH{=}CHPPh_2$) as the catalyst precursor in 1-pentene hydroformylation at 130 °C and 40 bar $H_2:CO = 1:1$ extensive cluster fragmentation is observed at the end of the hydroformylation reaction based on the isolation of the initially charged cluster in $<10\%$ yield. Cylindrical internal reflectance spectroscopy has been used to study the stability of the $PhCCo_3(CO)_7(L\text{-}L)$ cluster and the nature of cluster fragmentation species present in the working catalyst solution. Cluster fragmentation to $[Co(CO)_4]^-$ occurs early in the reaction, prior to alkene hydroformylation, followed by the formation of the phosphine-substituted complexes $[Co(CO)_3(L\text{-}L)]^+$ and $[Co(CO)_2(L\text{-}L)]^-$ [2].

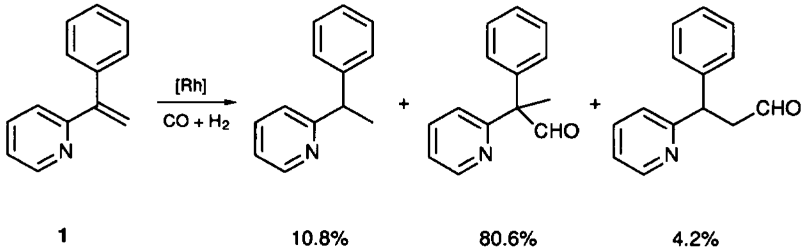
Cobalt tetrakis(diphenylphosphino)neopentane was found to have a high activity for hydroformylation of olefins. Comparison with cobalt–bisphosphine catalysts gaved the catalytic activities in the following decreasing order: $C(CH_2PPh_2)_4 \approx Ph_2P(CH_2)_2PPh_2 > Ph_2P(CH_2)_3PPh_2 > Ph_2P(CH_2)_4PPh_2$ [3].

The effects of alkali additives on cobalt–phosphine catalysts under hydroformylation conditions were studied by in situ IR spectroscopy. It was found that using potassium acetate as additive, the conversion of olefins and yield of alcohols are higher, but more alkanes and isoolefins are produced [4].

Bis(diphenylphosphine)propane–dicobalt hexacarbonyl complex was used as catalyst precursor in hydroformylation of 1-heptene in the range of 110–150 °C and 30–60 bar [5]. See also Refs. [6,16,49,50–52].

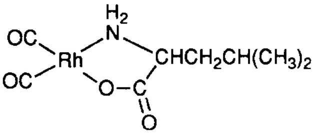
1.1.2. Rhodium catalysts

The hydroformylation of **1** in benzene solution at 80 °C under 100 bar $CO:H_2 = 1:1$ using $HRh(CO)(PPh_3)_3$ as the catalyst precursor resulted in a good yield of the predominantly branched aldehyde. Other rhodium, platinum and cobalt complexes were found to exhibit lower catalytic activity towards hydroformylation, the hydrogenation of the substrate being in those cases the main reaction [6].



$HRh(CO)(C_{60})(PPh_3)_2$ has been synthesized by allowing the hydroformylation catalyst, $HRh(CO)(PPh_3)_3$, to react with an equimolar amount of C_{60} in toluene. This compound was found to be an efficient catalyst for the hydroformylation of alkenes to aldehydes at 90 °C. The activity and regio-specificity for the conversion of propene, CO and H_2 to butanol are only slightly lower compared with $HRh(CO)(PPh_3)_3$, however, $HRh(CO)(C_{60})(PPh_3)_2$ in the presence of CO and H_2 shows greater thermal stability than the $HRh(CO)(PPh_3)_3$ [7].

Hydroformylation of styrene using chelate rhodium complexes such as **2** and diphosphine ligands at 60 °C and 1 bar showed that dppe ($Ph_2PCH_2CH_2PPh_2$) and dppm ($Ph_2PCH_2PPh_2$) can induce a higher catalytic activity and regioselectivity to the branched aldehyde $PhCH(CH_3)CHO$, than Ph_3P, whereas $(PhO)_3P$ promoted the formation of $PhCH_2CH_2CHO$. Increasing the P/Rh ratio led to a decrease of the initial activity, but higher conversion [8].



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Hydroformylation of vinylarenes, alkenes, and cyclic olefins has been investigated using (1,5-cyclooctadiene)salicylaldoximatorhodium, [Rh(SOX)(COD)], as catalyst precursor at 1 bar and 60°C in toluene. The anionic salicylaldoximato chelate ligand plays an important role in determining the hydroformylation activity under mild conditions. The reaction rate and regioselectivity also depend on the phosphine or phosphite ligand added. The combination of Rh(SOX)(COD) with diphosphine ligands is more active in the hydroformylation of vinylarenes, but those with monophosphine ligands are favored in the hydroformylation of alkenes. The use of diphosphine increases the formation of branched aldehydes in the hydroformylation of both vinylarenes and alkenes. Increasing the phosphine concentration results in a decrease of catalytic activity, but the regioselectivity remains almost constant in all cases [9]. The catalytic activity of $[Rh(CO)_2(LL)]$ and [Rh(COD)(LL′)] (LL′ = salicylaldoximate, 8-quinolinolate, glycinate, leucinate, aminophenolate, pyridinecarboxylate) in the hydroformylation of styrene was studied at 60 °C in toluene solution at atmospheric pressure of $CO:H_2 = 1:1$. It was found that these complexes, combined with dppp : Rh = 25 (dppp = $Ph_2PCH_2CH_2CH_2PPh_2$) exhibit high activity in the chenoselective styrene hydroformylation, leading to almost 100% yield of predominantly (97.6% in the best case) the branched aldehyde [10].

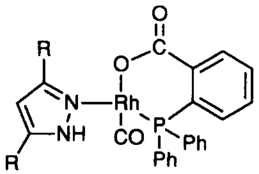
The 1,8-bis(diphenylphosphino)-3,6-dioxaoctane (dppoo) rhodium complex $[(dppoo)Rh(COD)][ClO_4]$ was found to show a low activity towards the hydroformylation of 1-hexene at 50 °C and 20 bar $CO:H_2 = 1:1$ in the presence of triethylamine [11].

The hydroformylation reaction of cyclopentene, cyclohexene, 4-vinylcyclohexene, cycloheptene and some cyclic dienes catalyzed with a $Rh(acac)\{P(OPh)_3\}_2/P(OPh)_3$ system at 80 °C and 10 bar $CO:H_2 = 1:1$ were studied. The main reaction products of 1,3- and 1,4-cyclohexadienes and 1,3-cyclopentadiene are unsaturated monoaldehydes. In hydroformylation of 1,5-cyclooctadiene the main product is formylcyclooctene [12].

The selectivity in rhodium-catalyzed hydroformylation was found to be kinetically controlled and determined by diphosphine chelation mode [13].

Hydroformylation of substituted styrenes, vinyl acetate and 3,3-dimethyl-1-butene at 25 °C was studied using $[Rh(COD)(O_2CR)]_2$ (R = Me, Ph_3C) as the catalyst precursor in the absence of phosphine or phosphite ligands. High yields and regioselectivities greater than 95:5 for branched:linear aldehydes from styrenes and vinyl acetate were obtained. Only the linear aldehyde was obtained with 3,3-dimethyl-1-butene [14].

The monorhodium (**3**) and the dirhodium complexes (**4**, **5**) were found to catalyze the hydroformylation of acyclic and cyclic olefins at 120 °C and 28 bar $CO:H_2 = 1:1$ pressures. At 70–90 °C, the dinuclear complexes with 3-(diphenylphosphino)benzoic acid moieties are more active than the monorhodium compounds [15].



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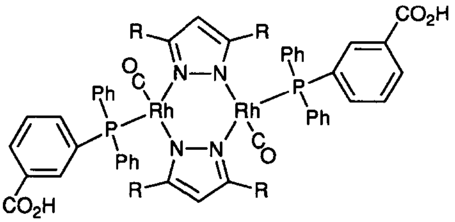

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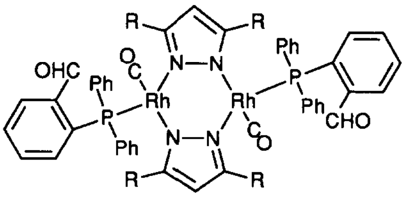


(R = H, CH_3)

5

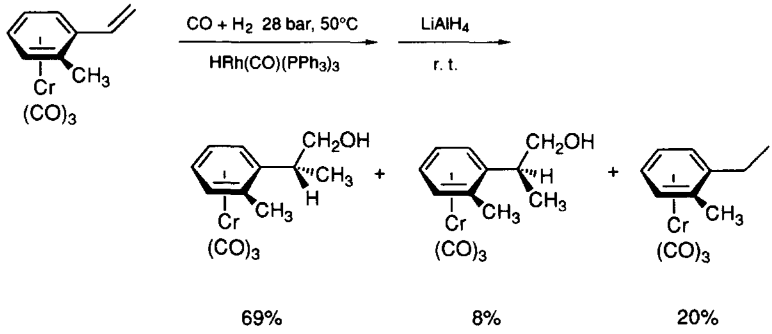
The hydroformylation of vinylsilanes using zwitterionic Co, Rh and Ir complexes was investigated. In the hydroformylation of vinyltrimethylsilane in the presence of $Rh(COD)BPh_4$ at 100 °C, 13 bar $CO:H_2 = 1:2$ give 2-(trimethylsilyl)-propanal selectively. The addition of $\geqslant 2$ equiv of PPh_3 causes a complete shift in the selectivity yielding the linear isomer as the major product [16].

The selectivity in the hydroformylation of 1-decene by homogeneous catalysis with $RhH(CO)(PPh_3)_3$ was studied. Aromatic solvents (benzene, toluene) gave total selectivity to aldehyde products, but alcoholic solvents gave higher n/iso ratios. The presence of an excess of phosphine also led to improved n/iso ratios [17]. The kinetics of hydroformylation of 1-decene using homogeneous $RhH(CO)(PPh_3)_3$

catalyst has been reported in the temperature range of 50–70 °C. The effect of catalyst, dihydrogen and carbon monoxide partial pressures and 1-decene concentration on the rate of hydroformylation have been studied. Based on the analysis of initial rate data, a rate equation has been proposed and kinetic parameters evaluated. The rate equation derived assuming oxidative addition of dihydrogen as a rate–determining step has been found to represent the data satisfactorily [18].

The effect of trivalent phosphorus compounds, such as phosphines and phosphites, on the activity and product selectivity of the rhodium complex-catalyzed hydroformylation of allyl alcohol was investigated. The observed normal/iso selectivity could be correlated with electronic and steric parameters of the phosphine ligands. Non-bulky phosphines such as $PMePh_2$ and PMe_2Ph gave high normal/iso product ratios [19].

The rhodium-catalyzed hydroformylation of *ortho*-substituted tricarbonyl(η^6-styrene)-chromium was found to occur with high regio- and diastereo-selectivities, e.g.

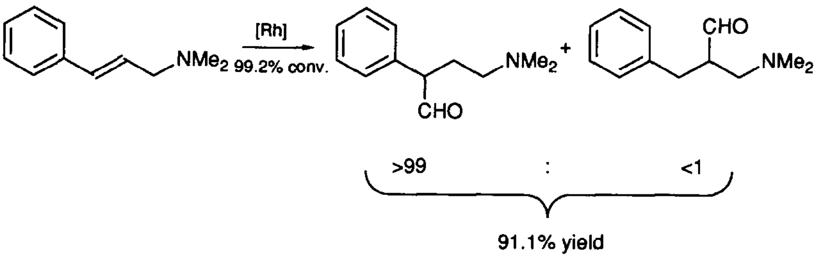


A similar regioselectivity was also observed with tricarbonyl (η^6-indene)chromium, but with lower diastereoselectivity [20].

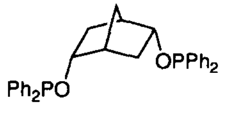
The effect of temperature and pressure on the hydroformylation of 1,5-hexadiene was studied using $Rh(acac)\{P(OPh)_3\}_2/P(OPh)_3$ and $Rh(acac)(CO)(PPh_3)/PPh_3$ as the catalyst precursors. The yields of dialdehydes were found to increase with temperature and pressure and reaches 100% at 80 °C and 10 bar of $CO:H_2=1$ using the $Rh(acac\{P(OPh)_3\}_2)/P(OPh)_3$ system. The reaction catalyzed by the $Rh(acac)(CO)(PPh_3)/PPh_3$ system produces, besides dialdehydes, monoaldehydes with a terminal double bond, namely 6-heptanal and 2-methyl-5-hexenal. The migration of the double bonds in monoaldehydes depends mainly on the donor properties of modifying ligands. Because of their strong donor properties phosphine ligands restrict isomerization (double bond migration) and diminish the yield of 4-heptenal. In contrast, when less strongly donating ligands such as phosphites are used as modifying ligands, 4-heptenal is the main reaction product [21].

Hydroformylation of allyl alcohol in the presence of in situ prepared rhodium complexes was studied. Correlation between the catalyst structure and selectivity of allyl alcohol hydroformylation was analyzed and the results were compared with those of propene hydroformylation [22]. Modification of $HRh(CO)(PPh_3)_3$ and dicarbonylrhodium acetylacetonate catalysts with sodium alkoxide was found to affect the rate and selectivity of hydroformylation of allyl alcohol and propene in alcoholic solution [23]. The hydroformylations of styrene, α-methylstyrene, *p*-methylstyrene and *p*-acetoxy-α-methylstyrene were carried out in the presence of a catalyst system containing $Rh(acac)(CO)_2$ modified with PPh_3 and phosphite ligands at 80 °C under 60 bar $CO:H_2 = 1:1$ pressure [24]. The hydroformylation of 2,3- and 3,5-dihydrofurans in the presence of dicarbonylrhodium acetylacetonate modified with various phosphites were studied. A quantum chemical treatment of the hydroformylation was given [25].

N-cinnamylamines were found to undergo a highly regioselective hydroformylation catalyzed by rhodium carbonyl phosphine complexes at 80 °C and 100 bar $CO:H_2 = 1:1$ in benzene solution [26], e.g.



The application of **6** and **7**, which have a natural bite angle around 120°, as ligands in the rhodium(I)-catalyzed hydroformylation of styrene and vinyl acetate was examined. The catalyst containing **6** or **7** was found to exhibit a high turnover frequency as compared with a typical 1,2-bis(diphenylphosphino)ethane with a bite angle around 85°. Using these ligands regioselective formation of 2-phenylpropanal (up to 97%) and 2-acetoxypropanal (>99%) was observed from styrene and vinyl acetate, respectively [27].



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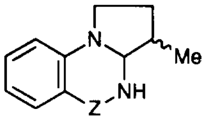
7

Rhodium-catalyzed reactions of *o*- or *p*-cyano-*N*-allylanilines with H_2/CO were found to give *N*-arylpyrrolidine aldehydes resulting from a double hydroformylation sequence [28]. The rhodium-catalyzed hydroformylation of a series of unsaturated thioethers, dithianes, dioxanes and dioxolanes was shown to give aldehydes in very good yields. The regioselectivity in some cases appears to be influenced by coordination between the rhodium catalyst and the sulfur substituent, especially when $Rh_4(CO)_{12}$ is used as the catalyst precursor [29]. Rhodium-catalyzed reactions of *o*-alkenylaminobenzylamines or -benzamides $CH_2{=}CR(CH_2)_nNHC_6H_4ZNH_2$ ($Z = CH_2$, CO; $n = 1, 2$; $R = H$, Me) with H_2/CO give quinazolines and quinazolinones containing a fused alicyclic ring in excellent yields. Reactions of *N*-allyl derivatives give readily separable mixtures of pyrrolo and pyrido derivatives **8** and **9** [30].



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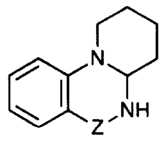

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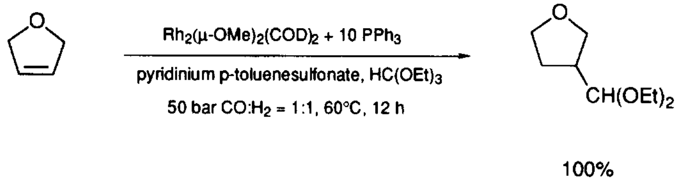
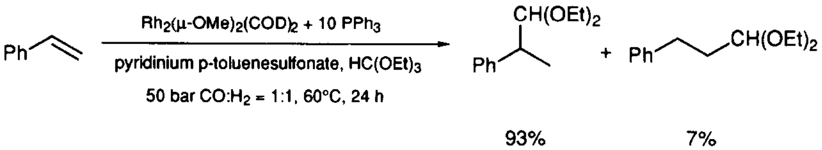
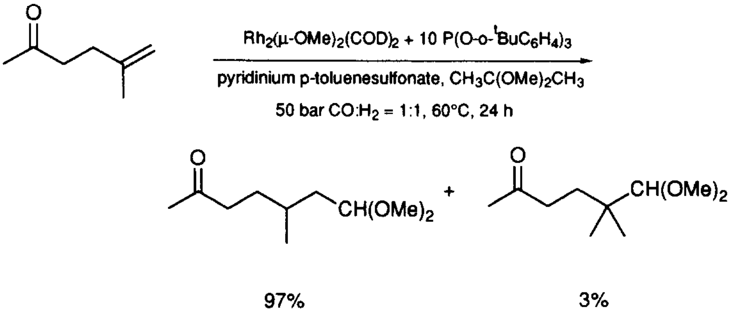
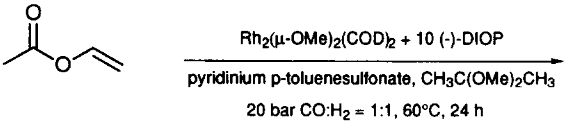
Mixed bidentate (P–N) ligands, e.g. $Ph_2P(CH_2)_2Py$ (Py = 2-pyridyl) and $Ph_2P(CH_2)_2N(CH_3)_2$ were found to enhance the rate of the rhodium-catalyzed hydroformylation of olefins. Branched/linear selectivities up to 98% were achieved in the hydroformylation of styrene at 80 °C and 40 bar $CO:H_2 = 1:1$ in chloroform solutions [31]. Mixed amino phosphine oxide ligands, e.g. $Ph_2P(O)CH_2NMe_2$, combined with $[RhCl(COD)]_2$ show high reactivity and selectivity for the formation of the branched aldehyde in styrene hydroformylation [32].

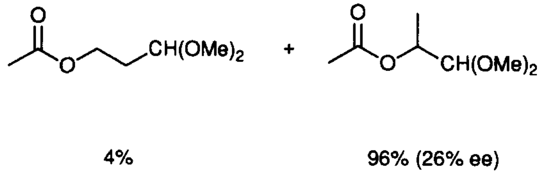
Efficient conversion of alkenes to acetals has been achieved by consecutive hydroformylation–acetalization reactions catalyzed by the rhodium complex $[Rh_2(\mu\text{-}OMe)_2(COD)_2]$ and pyridinium *p*-toluenesulfonate or by a zwitterionic rhodium catalyst $[Rh_2(\mu\text{-}S(CH_2)_3NMe_2H)_2(COD)_2][PF_6]_2$ [33], e.g.



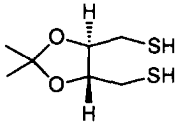






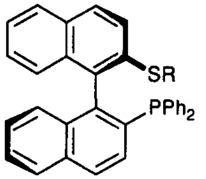


Asymmetric hydroformylation of styrene has been studied using the bridged dithiolate chiral rhodium complexes $[Rh_2(\mu\text{-}(-)\text{-DIOS})(COD)_2]_n$ ($n = 1$ and 2; (−)-DIOS = **10**) as the catalyst precursors. The catalytic systems provide high conversion in the corresponding aldehydes (100% at 30 bar and 65°C) with a selectivity in 2-phenylpropanal of 64%, which was increased to 91% by the addition of triphenylphosphine to the catalytic system. The enantiomeric excess, however, was very low (3%–5%). By the addition of a four-fold molar excess of (+)-DIOP instead of triphenylphosphine to the $[Rh_2(\mu\text{-}(-)\text{-DIOS})(COD)_2]$ to the catalyst precursor the enantiomeric excess in (*S*)-phenylpropanal was improved to 17% [34].



10

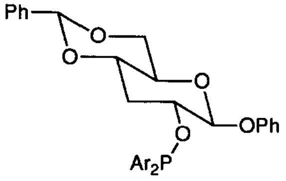
Rhodium complexes containing **11** as a ligand catalyze the asymmetric hydroformylation of styrene. The best result, 96% regioselectivity of the branched aldehyde and 14% enantiomeric excess at 40 °C and 120 bar $CO : H_2 = 1 : 1$, was obtained with the ligand with $R = {}^{i}Pr$ [35].



$R = Me, {}^{i}Pr$

11

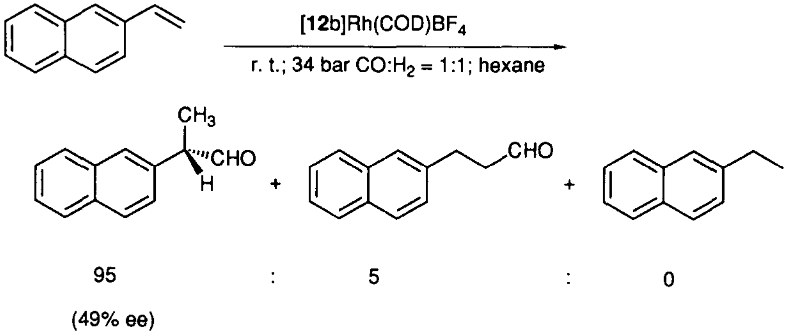
Carbohydrate vicinal diphosphinites (**12**) were used as highly tunable ligands in rhodium-catalyzed hydroformylation of olefins.



a. $Ar = C_6H_5$
b. $Ar = 3,5\text{-}(CF_3)_2C_6H_3$
c. $Ar = 3,5\text{-}F_2C_6H_3$
d. $Ar = 3,5\text{-}(CH_3)_2C_6H_3$

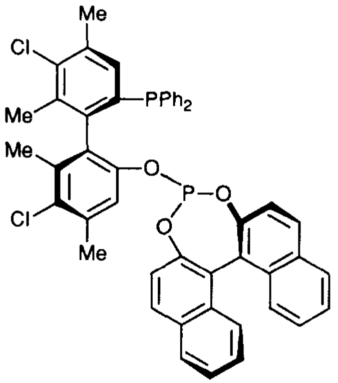
12

Substitution of electron-withdrawing aryl groups at phosphorus in these diphosphinites increased the enantioselectivity of the hydroformylation process. Very high branched-to-linear ratios of product aldehydes (>94%) were obtained, e.g.

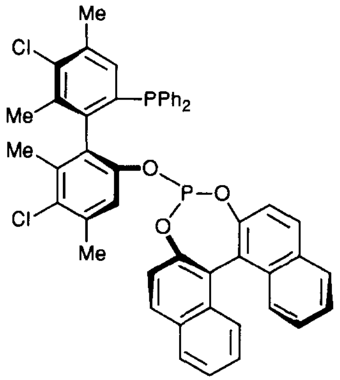


Using triethylsilane as the solvent in the above reaction the enantioselectivity increased to 72% enantiomeric excess [36].

Rhodium(I) complexes of the new chiral phosphinephosphites (*R*,*S*)-**13** and its enantiomer (*S*,*R*)-**13** were found to be highly efficient catalysts for asymmetric hydroformylations of a variety of olefinic substances at 60 °C and 100 bar CO : H_2 = 1 : 1 in benzene solution.

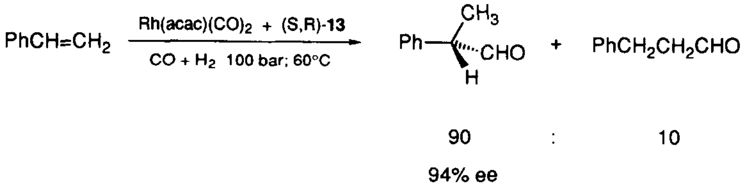


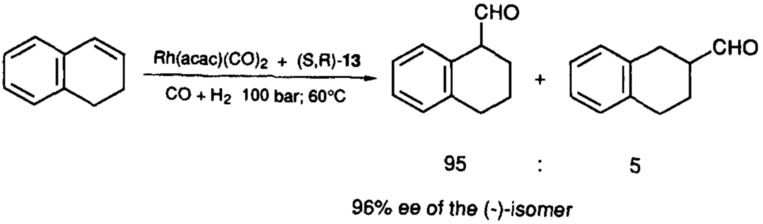
(R,S)-**13**



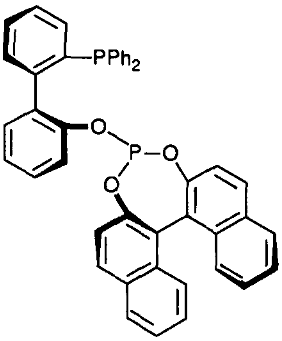
(S,R)-**13**

e.g.

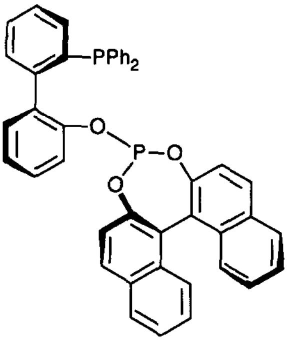




The corresponding phosphinephosphites derived from 2,2′-biphenyldiol in form of a 55:45 mixture of (*S*,*R*)-**14** and (*R*,*R*)-**14** were also tested as ligands for asymmetric hydroformylation. For all of the tested substrates, the regioselectivity and enantiomeric excess were found to be almost the same or even higher compared with those obtained by use of (*R*,*S*)-**15** or (*S*,*R*)-**15** [37].

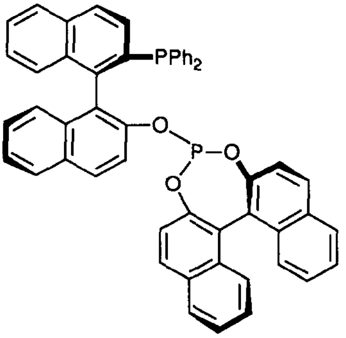


(S,R)-**14**

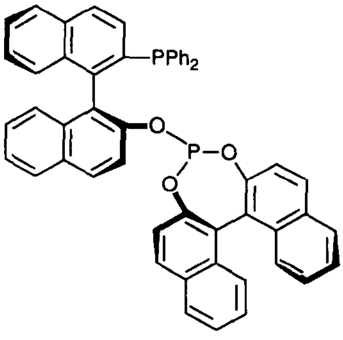


(R,R)-**14**

Hydroformylation of internal olefins such as (*E*)- and (*Z*)-but-2-ene, (*E*)- and (*Z*)-1-phenyl-prop-1-ene, indene and 1,2-dihydronaphthalene catalyzed by (*R*,*S*)-**15** or its enantiomer (*S*,*R*)-**15** gave the corresponding aldehydes in high enantiomeric excess. For example, *S*-(+)-2-methylbutanal was obtained in 82% ee and in the case of 1,2,3,4-tetrahydronaphthalene-1-carbaldehyde up to 97% ee was achieved [38].

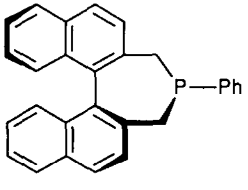


(R,S)-**15**



(S,R)-**15**

Atropisomerically pure (*S*)-**16** as the chiral ligand was found to be effective for the asymmetric hydroformylation of styrene with rhodium catalysts. At 60 °C in benzene solution using styrene: (*S*)-**16**:Rh = 500:4:1 and CO:H_2=1:1 at 50 bar pressure the reaction was found to be completely chemoselective towards aldehydes at 96% conversion. The branched isomer accounts for 93% of the product with 12% enantiomeric excess of the *R*-enantiomer [39] (see also Refs. [56,58]).



(S)-**16**

1.1.3. Other metals as catalysts and bimetallic catalysts

A correction of the article 'Influence of the reaction temperature on the enantioselection of styrene hydroformylation catalyzed by $PtCl(SnCl_3)$ complexes of *p*-aryl-substituted chiral ligands', Organometallics, 12 (1993) 848, has appeared [40].

The hydroformylation of styrene using the catalyst mixture $PtCl_2$/(P-P)/$SnCl_2$ (P-P=$[(R_2PCH_2)_2NR']PF_6$; R=Ph or ^{c}Hex, R′=*D*-(+)-CHMePh, *L*-CHMe-CO_2Et, (*R*)-(+)-bornyl) show asymmetric induction with up to 31% enantiomeric excess of 2-phenylpropanal being observed [41].

The complexes $[Ru(Ph_2PPy)_3Cl][Rh(CO)_2Cl_2]$ and $[Ru(Ph_2PPy)_3Cl][Ir(CO)_2Cl_2]$ were used as catalysts in the hydroformylation of styrene. An almost quantitative conversion of styrene was observed under 50–60 bar CO:H_2=1:1 and 75 °C in 6 h. The branched isomer aldehyde predominates in all experiments and its amount increases upon reducing the reaction temperature. At 40 bar the branched/linear ratio improves from ≈2.3 to 18 operating at 100 and 45 °C, respectively. The heterobimetallic Ru–Rh complex was found to be a more active catalyst in hydroformylation than mononuclear $[Ru(Ph_2PPy)_3Cl]Cl$ and $AsPh_4[Rh(CO)_2Cl_2]$. This was explained by a cooperative effect between the anionic rhodium and cationic ruthenium species in the Ru–Rh complex. The Ru–Ir complex as precatalyst showed only negligible activity [42].

Hydroformylation reactions of a series of alkenes and alkynes have been carried out using the heteronuclear rhodium–tungsten catalyst, $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Rh}H(CO)(PPh_3)$. The results of these reactions have been compared with corresponding reactions using $[Rh(OAc)_2]_2$ as the catalyst precursor. Reactions of the phosphinoalkene, $Ph_2P(CH_2)_3CH{=}CH_2$ and the corresponding alkyne, $Ph_2P(CH_2)_3C{\equiv}CH$ gave similar products using either catalyst system with the alkyne reaction being significantly slower. Catalysis of a reaction of styrene using a rhodium–tungsten catalyst gave a very high yield of the branched chain aldehyde containing only a trace of the straight chain isomer. Reaction of the alkenyl dithiane, 3-(1,3-dithian-2-yl)-prop-1-ene, using the rhodium–tungsten catalyst gave a higher ratio of linear to branched aldehydes than the corresponding reaction using $[Rh(OAc)_2]_2$. Reactions of allyl acetate gave similar products for both catalytic systems [43].

Bimetallic catalytic hydroformylation has been the topic of a dissertation [44]. See also Refs. [6,16,45–47,49–52,60].

1.2. Heterogeneous systems

1.2.1. Supported complexes

Triruthenium dodecacarbonyl/2,2′-bipyridine/SiO_2 catalyst has been prepared by a new pulse impregnation and the effect of the preparation method on the catalyst activity was tested in 1-hexene hydroformylation [45]. The stability of the supported triruthenium dodecacarbonyl/2,2′-bipyridine catalysts was studied by determining the ruthenium content of hydroformylation products and also by special dissolution tests. Ruthenium was found to dissolve in hydroformylation products, however, the nature of the catalyst proved to be mainly heterogeneous [46].

Stoichiometric acetaldehyde formation by insertion of CO into the methyl ligand and catalytic ethene hydroformylation on the cluster, $[Ru_6C(CO)_{16}Me]^-$ supported on silica at 373–473 K were investigated to understand the effects of the catalysis on the metal cluster framework and also to develop new catalytic systems on a molecular scale. The reaction of the cluster framework under the reaction conditions was confirmed by extended X-ray adsorption fine structure curve-fitting analysis. On the contrary $[Ru_6C(CO)_{16}Me]^-$ in a homogeneous system did not catalyze this reaction and conventional impregnation ruthenium–silica catalysts showed only 0%–0.09% selectivity [47].

The structure of the cluster framework in tetrarhodium dodecacarbonyl attached to tris(hydroxymethyl)phosphine-modified silica was studied by EXAFS and IR spectroscopies in conjunction with their catalytic activities and selectivities in the olefin hydroformylation reaction [48].

Silica-supported poly(γ-aminopropylsiloxane)CoRu complex was prepared and used to catalyze the hydroformylation of cyclohexene with >90% conversion. Cyclohexanecarbaldehyde was initially formed, followed by reduction to cyclohexanemethanol [49]. Selective hydroformylation of styrene to 2-phenylpropionaldehyde in higher than 90% yield has been achieved using silica-supported poly(γ-aminopropylsiloxane)CoRu bimetallic complex catalysts in the presence of acetic acid [50].

The polymer-supported heteropentametallic cluster $FeCo_3(CO)_{12}(\mu_3\text{-}AuPPh_2\text{-}CH_2C_6H_4\text{-Polymer})$ was found to be a good catalyst for hydroformylation of olefins [51]. Polymer supported iron–cobalt tetrametallic clusters have been used as catalysts in the hydroformylation of 1-hexene. Heptaldehyde yields of 83.2%–92.4% and normal/iso ratios of 1.2–1.6 were reported [52].

Phosphine ligands with polar substituted groups as well as their rhodium carbonyl complexes have been attached to modified silica substrates. The efficiency of immobilization has been tested in hydroformylation reactions of several olefins (2-(±)-ethylhexyl acrylate, sodium 10-undecenoate, ethyl 10-undecenoate, 1-vinylimidazole) using both hydrophobic (cyclohexane) and hydrophilic (water) reaction media [53]. Activities of rhodium complex catalysts containing Ph_2P derivatives of polystyrene, polybutadiene, or poly(vinyl) chloride as ligands were compared in hydroformylation of dodecene in solution at 90° C under 10 bar $CO-H_2=1:1$ pressure. The most effective catalyst contained three phosphorus-attached aryl groups. Increasing the content of Ph_2P groups on the polymer chain resulted in an increased yield of n-tridecanol in the case of the polystyrene derivative, and decreased hydroformylation rate in the case of the polyvinylchloride and polybutadiene derivatives [54]. The activity and regioselectivity of a rhodium complex of phosphinated polystyrene in the hydroformylation of 1-dodecene were studied [55] and the results were compared with those obtained in the case of the $HRh(CO)(PPh_3)_3+PPh_3$ catalytic system [56].

The $RhCl(PPh_3)$ complex exchanged with modified montmorillonite clay at room temperature gave a $[Rh(PPh_3)_3]^+$ species anchored in the hydration layers of the clay. Hydroformylation of allyl alcohol catalyzed by $[Rh(PPh_3)_3]^+$/montmorillonite at 70 °C and 60 bar $CO:H_2=1:1$ gave γ-hydroxybutyraldehyde (96%) and 2-methyl-3-hydroxypropionaldehyde (4%). The kinetics of hydroformylation of allyl alcohol was studied in the concentration range of catalyst 0.1 to 0.75 mM, allyl alcohol 0.025 to 0.25 M, $CO:H_2=1:1$ pressure 5–30 bar and temperature between 70 and 90 °C. The rates of hydroformylation of allyl alcohol showed a first order dependence with respect to catalyst, allyl alcohol (up to 0.1 M), and H_2 concentrations, respectively. Although carbon monoxide showed an obvious negative effect on the conversion, the mechanistic conclusions has been based erroneously on a first order dependence [57]. The catalytic activity of $RhCl(PPh_3)_3$ anchored on montmorillonite clay in hydroformylation of olefins at 70 °C and 60 bar $CO:H_2=1:1$ was investigated. The catalytic activity of the anchored catalyst was compared with that observed with Wilkinson's catalyst in solution under the same hydroformylation conditions [58].

Sulfonated poly(phenylene sulfide)–rhodium complexes supported on active-carbon were used as catalysts in hydroformylation of methyl ω-undecenoate in organic phase system [59].

The atmospheric hydroformylations of ethene and propene were investigated over silica-supported $Rh_4(CO)_{12}$, $Co_2(CO)_8$, $Co_2Rh_2(CO)_{12}$, $RhCo_3(CO)_{12}$-derived catalysts. The bimetal cluster-derived catalysts showed excellent activities for the formation of oxygenates. A subcarbonyl bimetal cluster is thought to be the actual catalytic species on the surface [60].

The hydroformylation of 1-hexene at 150 °C and 40 bar $CO:H_2=1:1$ in toluene using soluble and zeolite supported iridium compounds was reported. The active species of immobilized catalyst formed in the reaction environment was investigated [61].

Silica-supported water-soluble sulfonated triphenylphosphine–rhodium complex was found to show excellent catalytic activity for the hydroformylation of methyl-10-undecenoate in a fixed-bed reaction system. The selectivity was stabilized in the range of 98%–99% and normal/iso ratio over 4.0 when the phosphorus/rhodium mol. ratio was 10–15. This immobilized catalyst also showed significant water loss during the reaction but the catalytic activity was unaffected. The ligands and central metal might be redistributed at the initial stage of the reaction to form active species with suitable water content in the fresh catalyst, and then the hydrophilic support held the water-soluble phosphines by hydrogen bonding of the hydrated sodium sulfonate group to the surface [62].

A series of olefin hydroformylations over supported aqueous-phase rhodium catalyst with the substitution of CO/D_2 for CO/H_2 were carried out to study the isotope effects of deuterium. The rate of aldehyde formation with CO/D_2 was found to be about 1.3 times faster than that with CO/H_2, indicating that the aldehyde formation shows noticable inverse deuterium isotope effect [63].

Phosphorus-31 NMR lattice relaxation times, T_1, for supported aqueous phase hydroformylation catalysts derived from $HRh(CO)(TPPTS)_3$ and TPPTS (TPPTS = trisulfonated triphenylphosphine trisodium salt) were found to be consistent with a liquid-like character for the supported aqueous phase. The T_1 for solid TPPTS is 1150 s while for TPPTS in a supported aqueous phase T_1 varies from 220 to 4.9 s. A T_1 of 4.9 s is close to the value obtained for TPPTS in solution and is observed at a H_2O/P ratio of 24.9. At this level of water content previously reported supported aqueous phase catalysts have shown maximum catalytic activity for the hydroformylation of olefins [64] (see also Refs. [65,86,88]).

1.2.2. Biphasic systems

The formally zwitterionic complex anions, $[Co(CO)_3(P((CH_2)_nC_6H_4\text{-}p\text{-}SO_3)_3)_2]^{5-}$ ($n = 1$, 2, 3 and 6), as the sodium salt have been used as precursors to water-soluble cobalt hydroformylation catalysts under two-phase and supported aqueous phase conditions. The tendency to form alcohol products is low with these complexes. The behavior of the catalysts is consistent with an active species that remains in water solution during the reaction and is not leached into the nonaqueous phase [65].

Salt concentration was found to have a considerable influence on the activity and selectivity of water-soluble hydroformylation catalysts derived from $Rh(acac)(CO)_2$ and the sulfonated phosphine, $P[C_6H_4(CH_2)_3C_6H_4SO_3Na]_3$. Addition of Na_2SO_4 or Na_2HPO_4 to the catalysts enhances both the rate and selectivity of the hydroformylation reaction in the case of 1-octene [66]. Water-soluble rhodium compounds prepared in situ from $Rh(acac)(CO)_2$ and 1,2-bis[bis(μ-sodiosulfonatophenyl)phosphino]ethane show poor activity but selectivity similar to that of $Rh(acac)(CO)_2$ and trisulfonated triphenylphosphine in the two-phase hydroformylation of 1-octene. Under two-phase reaction conditions normal/branched ratios of 2.3–3.2 were observed for the hydroformylation of 1-octene at 120 °C and 14 bar of CO/H_2. Conversions in the range of 5%–25% were observed. Maximum activity was found at a P/Rh ratio of 3:1 [67]. The reaction selectivity in the aqueous phase rhodium-catalyzed hydroformylation of 1-octene with trisulfonated tris(ω-phenyl)alkylphosphines and trisulfonated triphenylphosphine were studied. Electron-donating water-soluble phosphines (L), $P[(CH_2)_xC_6H_4\text{-}p\text{-}SO_3Na]_3$, ($x = 1$, 2, 3, 6) were used to generate aqueous rhodium catalysts. At low L/Rh ratios, conversion generally increases with increasing number of CH_2 groups. At high L/Rh ratios the catalytic activity decreases. For comparison, data are given for $P(C_6H_4\text{-}\mu\text{-}SO_3Na)_3$ as well [68].

The catalytic activities and selectivities of water-soluble rhodium complexes

($RhCl(CO)(TPPTS)_2$, $HRh(CO)(TPPTS)_3$, and $RhI(CO)(TPPTS)_2$) in 1-hexene hydroformylation were studied in biphasic catalytic system at 100 °C and 10 bar $CO:H_2=1:1$. The turnover frequency was ≈40 mol/mol Rh min and the normal/iso ratio of aldehyde was over 4/1 [69].

A new type of water-soluble phosphine, $P[PhO(CH_2CH_2O)_nH]_3$ ($n=3$–14) was prepared and their rhodium complexes, formed in situ, were used in hydroformylation of 1-hexene, 1-octene, and 1-dodecene in a two-phase system. The best yield in the case of 1-dodecene was 85% [70].

A new water-soluble rhodium catalyst, rhodium-poly(*N,N*-diallyl-*N*-methylamine dihydrophosphate) complex was found to show high activity and stability in hydroformylation of 1-hexene [71].

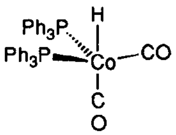
The rate and selectivity enhancement with surface-active phosphines was studied in the two-phase hydroformylation reaction of octene-1 with rhodium complexes. Rhodium catalysts derived from the new phosphines $P[C_6H_4(CH_2)_mC_6H_4\text{-}p\text{-}SO_3Na]_3$ ($m=3$, 6) show significant improvement over catalysts generated from trisulfonated triphenylphosphine, with respect to faster initial rates and better normal/branched ratio [72].

The biphasic hydroformylation of 1-octene, by using the water-soluble dinuclear complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ as the catalyst precursor was investigated at 80 °C and 5 bar $CO:H_2 = 1:1$. It was found that addition of ethanol as a cosolvent dramatically improved the yields but the good regioselectivity in linear aldehyde observed for neat 1-octene–water systems (96%) decreased to 83% (for 22% ethanol w/w) [73].

1.3. Coordination chemistry related to hydroformylation

Hydrogen atom transfer and related dynamic processes in oxo catalysis have been investigated by high-pressure ^{59}Co NMR spectroscopy [74].

The structures of both a trigonal bipyramidal form (**17**) and a square-pyramidal form (**18**) of dicarbonylbis(triphenylphosphine)cobalt hydride were determined by low temperature X-ray diffraction from two crystals grown in acetonitrile in the same crystallization [75].



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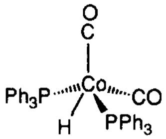


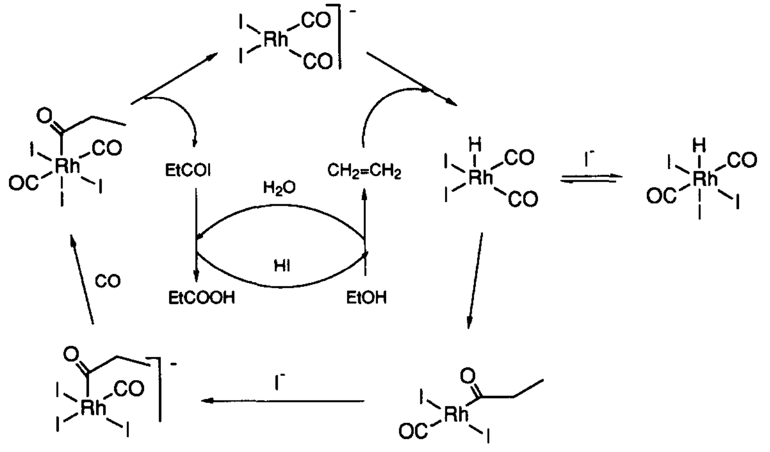
18

The equilibrium between an acylcobalt tetracarbonyl on one side and an alkylcobalt tetracarbonyl and carbon monoxide on the other has been determined using the acetyl- and methylcobalt tetracarbonyl couple in the 0–100 °C temperature range. The decarbonylation of acetylcobalt tetracarbonyl was found to be endothermic

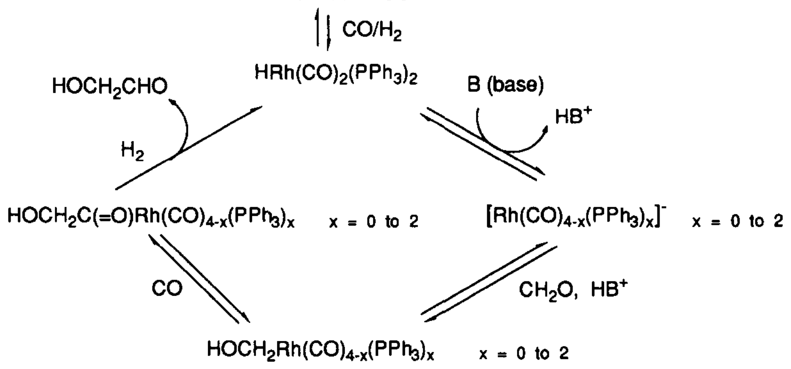
($\Delta H = 11.2 \pm 0.6$ kcal mol^{-1}) and is accompanied by a positive entropy change ($\Delta S = 19.5 \pm 2.0$ e.u.) [76].

The kinetics and mechanism of the methanolysis of acetylcobalt tetracarbonyl were studied. The rate of acetylcobalt tetracarbonyl methanolysis between 40 and 60 °C was found to be first-order with respect to the acetylcobalt tetracarbonyl concentration and independent of the carbon monoxide concentration. Nucleophilic substitution of $Co(CO)_4$ on the acyl-carbon by methanol was suggested as the most probable pathway [77].

A mechanism for the carbonylation of ethene to propionic acid using $[HRh(CO)_2I_3][AsPh_4]$ as the catalyst precursor was proposed where many of the proposed intermediates have been spectroscopically observed for the first time [78].



The catalytic cycle for the hydroformylation of formaldehyde to glycolaldehyde based on the understanding of a novel anionic reaction mechanism was elucidated through in situ spectroscopic studies and the synthesis and characterization of model intermediates. Thus, a key model rhodium acyl intermediate $CH_3OCH_2C(=O)$-$Rh(CO)_2(PPh_3)_2$ was synthesized, which, upon hydrogenolysis, gave the model product CH_3CH_2CHO and regenerated the catalyst [79,80].



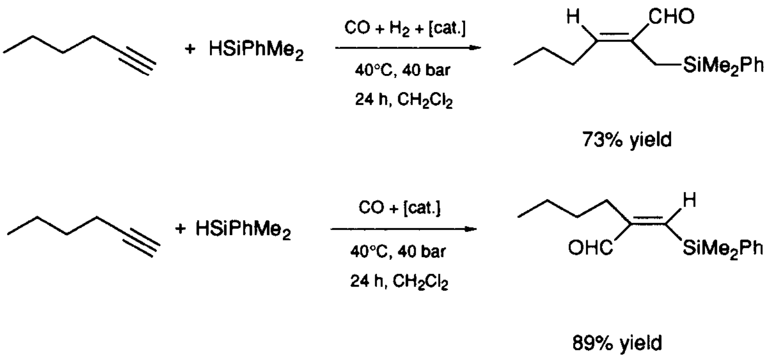
When iridium complexes were used as models, all important catalytic intermediates including the anionic catalyst ($[Ir(CO)_3PPh_3]^-$), the iridium alkyl species ($CH_3OCH_2Ir(CO)_2(PPh_3)_2$), and the iridium acyl species ($CH_3OCH_2C(=O)Ir(CO)_2(PPh_3)_2$), were synthesized and characterized [81].

2. Hydroformylation related reactions of CO

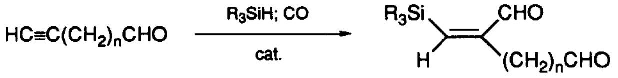
2.1. *Homologation, silylhydroformylation and silylformylation*

The catalytic synthesis of ethanol from aqueous methyl formate has been investigated using a catalyst system composed of triruthenium dodecacarbonyl, tri-n-butylphosphine, hydrogen chloride, and an onium salt such as PPNCl (PPNCl = bis(triphenylphosphoranylidene)ammonium chloride). Without using initial pressurization the yield of ethanol formation was found to be 22.5% at 200 °C, and 28.4% at 240°C. A mechanism was suggested which involves $HRu_3(CO)_{11}^-$ and the homologation of the methyl group in methyl formate [82].

The zwitterionic rhodium complex $[\eta^6\text{-}C_6H_5BPh_3]^-[Rh(COD)]^+$ was found to catalyze the reaction of alkynes with hydrosilanes and synthesis gas ($CO:H_2 = 1:1$) at 40°C. The term 'silylhydroformylation' has been used to describe these transformations in contrast with the silylformylations which are performed in the absence of H_2 [83].



Extremely chemoselective silylformylation of alkynals were observed using various hydrosilanes in the presence of $[Rh(CO)_2Cl]_2$, $[Rh(NBD)Cl]_2$, $[Rh(COD)Cl]_2$, $Rh(acac)(CO)_2$, $Rh_2Co_2(CO)_{12}$, $(^tBuNC)_4RhCo(CO)_4$, and $[Rh(NBD)_2]BF_4$ as the catalyst precursor (0.5 mol%) at 25°C and 10 bar of carbon monoxide in toluene. The alkynals **19** gave the corresponding (*Z*)-2-(silylmethylene)-1-ω-dialdehydes **20** as the sole products of the reaction in high isolated yields. Yields determined by NMR are ≈95% in all cases [84].



19 **20**

n = 3, 4, or 5

R_3 = $PhMe_2$, Et_3, $^tBuMe_2$, Ph_2Me, Ph_3

The silylformylation of alkynes to form β-silylacrylaldehydes was found to occur efficiently in the presence of dirhodium(II) perfluorobutyrate with turnover numbers that exceed 300. Reactions take place at atmospheric pressure and 0 °C by controlled addition of the alkyne to the combination of organosilane and $Rh_2(C_3F_7COO)_4$ or at 10 bar of carbon monoxide without this control [85], e.g.

$$\mathrm{PhC{\equiv}CH + Me_2PhSiH \xrightarrow[10\ bar\ CO]{[Rh]} Me_2PhSiCH{=}C(Ph)CHO}$$

Z:E = 12:1, 73% yield

$$\mathrm{6\text{-}MeONapht\text{-}2\text{-}C{\equiv}CH + Et_3SiH \xrightarrow[10\ bar\ CO]{[Rh]} Me_2PhSiCH{=}C(2\text{-}Napht\text{-}6\text{-}MeO)CHO}$$

Z:E = 21:1, 99% yield

2.2. Water gas shift reaction

Supported triruthenium dodecacarbonyl and 2,2-bipyridine catalysts were prepared by controlled deposition from the gas phase on amorphous supports and were tested in 1-hexene hydroformylation and the water gas shift reaction. In the latter reaction the the highest activities were 2–2.5 times greater than those obtained with catalysts prepared by impregnation [86].

The reverse water gas shift reaction ($H_2+CO_2 \rightarrow H_2O+CO$) was homogeneously catalyzed by an anionic ruthenium cluster in the presence of bis(triphenylphosphoranylidene)ammonium chloride at 160 °C. The catalytic reaction was estimated to proceed via dehydrogenation of hydride cluster, followed by coordination of CO_2 and electrophilic attack of the proton on its oxygen atom in the presence of chloride anion [87].

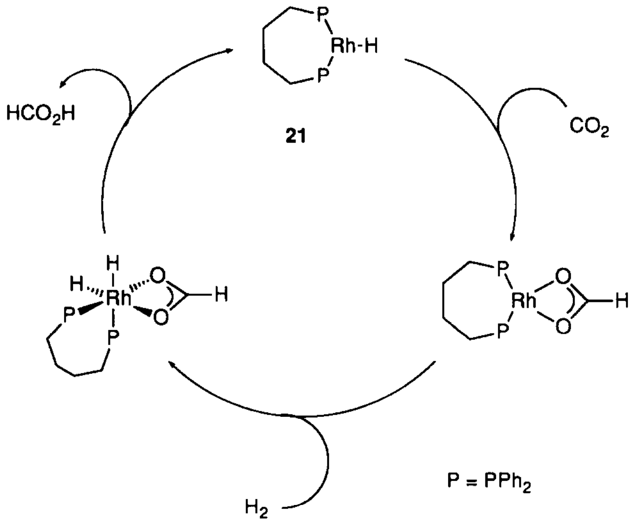
Catalysts for the water gas shift reaction from $RhCl_3 \cdot 3H_2O$ immobilized on several porous aminated polymers in neutral aqueous and aqueous organic solvent media have been investigated. Those using poly(4-vinylpyridine) as the support proved to be the most active. The turnover frequencies for the production of dihydrogen were found to display a nonlinear dependence on the partial pressure of carbon monoxide in the 0–1.5 bar range, but were found to be independent of the polymer loading in the range $0.5\text{–}1.5 \times 10^{-4}$ mol $RhCl_3 \cdot 3H_2O$ per g of polymer. The activity of the poly(4-vinylpyridine)-anchored catalyst was found to be insensitive to pH in the 3–5 zone but to fall off sharply outside this range. This species also catalyzes hydrogenation and hydroformylation of alkenes [88].

The water gas shift reaction catalyzed by heterogeneous solutions of $IrCl_3 \cdot 3H_2O$ and $RhCl_3 \cdot 3H_2O$ supported on aminated styrene-divinylbenzene copolymer resins and on poly(4-vinylpyridine) was studied in ethoxyethanol/water = 8/2 (vol/vol) under 0.9 bar carbon monoxide pressure and at 100 °C. The highest turnover frequencies of hihydrogen production were observed in the case of the poly(4-vinylpyridine) support [89].

The homogeneous water gas shift reaction using $Rh_4(CO)_{12}$ as the catalyst precursor was studied in aqueous pyridine solution at 80 °C, $P_{CO} = 1$ bar, and $[Rh] = 0.02$ M. A maximum turnover frequency of 172 mol H_2 per mol Rh d^{-1} was achieved in pyridine containing 3% water in the presence of an acid ($CF_3SO_3H/Rh = 10$) [90].

2.3. Reduction of CO_2

An efficient catalytic system for the rhodium-catalyzed reversible formation of formic acid from carbon dioxide and dihydrogen was reported. Thus, a rhodium catalyst formed in situ from $[\{Rh(COD)(\mu\text{-}H)\}_4]$ and $Ph_2P(CH_2)_4PPh_2$ in DMSO/Et_3N (5:1) converts carbon dioxide and dihydrogen into formic acid at room temperature and 40 bar. Up to 2200 moles of formic acid were formed per mole of rhodium with turnover frequencies as high as 375 h^{-1} in the best case. The diphosphine–rhodium(I) hydride species **21** was suggested to be the catalytically active intermediate in the proposed catalytic cycle [91].



Electropolymerized films of vinyl-terpyridine complexes of Fe, Ni and Co were found to exhibit electrocatalytic activity towards the reduction of carbon dioxide. In the case of electropolymerized films of $[Fe(vinyl\text{-}terpyridine)_2]^{2+}$, electrocatalysis for carbon dioxide reduction was observed at potentials below −1.0 V, which represents about 1 V diminution of the overpotential [92].

3. Reviews

Synthesis and catalytic application of cobalt and iron carbonyls; hydroformylation and related reactions. A review with 49 references of research on metal carbonyls from 1951 to 1993 in Veszprém, Hungary. Topics discussed include the preparation of more than 80 novel cobalt and iron carbonyl derivatives and their application in catalytic olefin hydroformylation. Mechanistic studies were emphasized, such as the partially radical character of the reaction, differences in reactivities for aliphatic and aryl-aliphatic olefins, isomeric composition of the aldehydes, and the presence of very reactive intermediates that cannot be isolated or detected spectroscopically [93].

Industrial oxo synthesis with immobilized catalyst. A review with 26 references on ten years of experience with large-scale oxo synthesis using the novel Ruhrchemie/Rhone Poulenc process and the $HRh(CO)[P(m\text{-}C_6H_4SO_3Na)_3]_3$ catalyst [94].

Development of a new catalytic process for manufacturing isononyl alcohol. A review with 13 references focused on the manufacturing of a mixture of isomeric C_9 alcohols by oxo reaction of mixed octenes followed by hydrogenation using the new rhodium–phosphine oxide catalyst [95].

Development of highly efficient catalysts for asymmetric hydroformylations. Rhodium(I) complexes coordinated with optically active phosphine–phosphite hybrid bidentate ligand BINAPHOS (see *R*,*S*-**15** and *S*,*R*-**15**) derived from optically active 1,1′-binaphthylene-2,2′-diol showed high performance in asymmetric hydroformylations of substituted olefins. This was given in a review with eight references [96].

Recent advances in asymmetric hydroformylations catalyzed by chiral platinum(II) and rhodium(I) complexes have been reviewed (19 references). Rhodium(I) complexes of BIPHEMPHOS (see *R*,*S*-**13** and *S*,*R*-**13**) are highly efficient catalysts for asymmetric hydroformylations of functionalized olefins, vinyl aromatic compounds and simple olefins. Preparation and use of similar ligands with chiral elements involving biphenyl frameworks are described [97].

A cooperative effect in Rh_2 complexes: high catalytic activity and high regioselectivity in hydroformylation of olefins has been studied in a review with eight references [98].

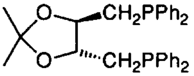
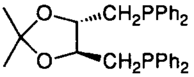
Asymmetric sunthesis using organometallic reagents, and nickel, palladium, and platinum complexes were described in a review on the recent progress in catalytic asymmetric reactions with more than 62 references [99].

High pressure reaction by homogeneous catalysis was covered by a review with 14 references principally on carbonylation and hydroformylation reactions as well as synthesis gas conversion [100].

Homogeneous catalysis with transition metal complexes was described in a review with 59 references of rhodium catalyzed hydroformylation, zirconium catalyzed polymerization of alkenes and enantioselective hydrogenation [101].

The life and contributions to chemistry of Otto Roelen was described, including his work on the Fischer–Tropsch synthesis, hydroformylation, and high-density polyethylene [102].

List of abbreviations

acac	acetylacetonate
COD	1,5-cyclooctadiene
(−)-DIOP	(2*R*,3*R*)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane 
(+)-DIOP	(2*S*,3*S*)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane 
DMSO	dimethylsulfoxide
dppp	$Ph_2PCH_2CH_2CH_2PPh_2$
dppoo	$Ph_2PCH_2CH_2OCH_2CH_2OCH_2CH_2PPh_2$
ee	enantiomeric excess
py	pyridine
r.t.	room temperature
TPPTS	tris(3-sulfonatophenyl)phosphine

Metal index

W	[43]
Fe	[51,52,92,93]
Ru	[42,45–50,82,83,86]
Co	[1–6,16,49–52,60,65,74–77,92,93]
Rh	[6–39,42,43,48,53–60,62-64,66–73,78–80,84,85,87–91,94–98,101]
Ir	[16,42,61,79–81,89]
Ni	[92,99]
Pd	[99]
Pt	[6,40,41,97,99]
Au	[51]

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