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Application of transition metals in hydroformylation annual survey covering the year 2002

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Contents

Abstract

Hydroformylation in homogeneous and heterogeneous systems, and hydroformylation related reactions of carbon monoxide reported in 2002 are reviewed.

Keywords: Hydroformylation; Silylformylation; Hydrocarboxylation; Alkoxycarbonylation; Hydroaminomethylation; Water–gas shift reaction; Reduction of carbon monoxide; Reduction of carbon dioxide; Transition metals

1. Hydroformylation

1.1. Homogeneous systems

1.1.1. Cobalt catalysts

The cobalt-catalyzed hydroformylation of 1,2-epoxyhex-5-ene (1) at 100 °C and 100 bar CO:H_2 = 1:1

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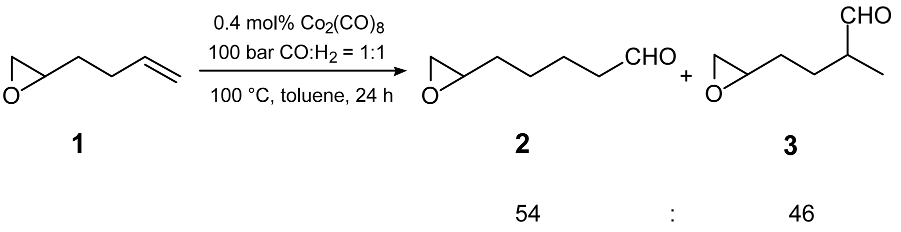


pressure was found to give the mixture of aldehyde isomers 2 and 3 in 99% yield [1].

It was found that the initial rate of $Co_2(CO)_8$-catalyzed cyclohexene hydroformylation and triethyl orthoformate carbonylation as well as the initial rate of $CoH(CO)_4$ formation from $Co_2(CO)_8$ and H_2 is reduced by the addition of dinitrogen, argon, or xenon. It is assumed that the additional gas competes with one or more reactants for a coordinatively unsaturated site responsible for their activation, thus affecting the reaction rate [2].

See also Ref. [85].

1.1.2. Rhodium catalysts

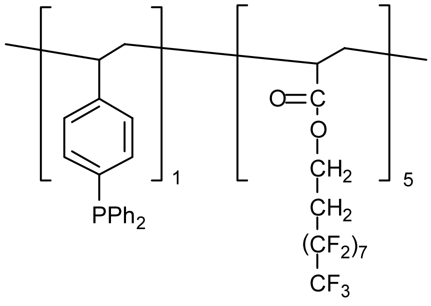
From analyses of the results of ^{2}H-NMR spectra of the products obtained in dimethylphenylphosphine-modified rhodium-catalyzed deuterioformylation of 4-vinyl-pyridine, the behavior of the alkyl rhodium intermediate during the reaction has been elucidated [3].

Directing abilities of alcohol-derived functional groups in the rhodium-catalyzed hydroformylation of olefins were investigated. The highest diastereoselectivity (*trans*:*cis* = 87:13) was observed in the reaction of 1-methoxymethoxy-2-methylenecyclohexane. Inherent conformational preferences were found to be of significant importance in determining the product distribution [4].

The effects of ammonium chromate, ammonium dichromate, ammonium molybdate and ammonium tungstate as additives on the catalytic performance of rhodium catalysts for the hydroformylation of C_8-olefins and 1-dodecene were investigated. Modification of the rhodium catalyst with ammonium salts resulted in moderate increase of the aldehyde yields and in decrease of rhodium losses in the distillation process for the separation of the products from the catalyst [5].

New chiral 2-menthylindenyl and 2-menthyl-4,7-dimethylindenyl rhodium complexes were tested among others in asymmetric hydroformylation of styrene. At 60 °C and 40 bar $CO:H_2 = 1:1$ practically no asymmetric induction was obtained [6].

Simple trialkylphosphines such as PEt_3 have been used as ligands in phosphine-modified homogeneous rhodium-catalyzed 1-hexene hydroformylation in super-



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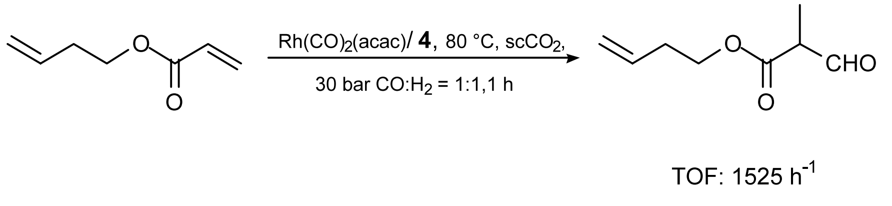


critical carbon dioxide. Above 200 bar total pressure at 100 °C heptanals are obtained with 97% selectivity. Under subcritical conditions, however, heptanols from hydrogenation of the first formed heptanals are the main products [7].

The hydroformylation reaction of ethylene using the (p-$CF_3C_6H_4)_3P$ ligand with the rhodium catalyst precursor $Rh(CO)_2(acac)$ in liquid CO_2 at 10 and 23 °C has been investigated by high-pressure NMR spectroscopy. ^{1}H-NMR was used to monitor the reaction progress of the hydroformylation and $^{31}P\{^1H\}$-NMR was used to identify potential resting states of the rhodium catalyst [8].

The combination of supercritical CO_2, $Rh(CO)_2(acac)$, and a fluorous polymeric phosphine **4** was found to be a highly effective catalytic system for the chemoselective hydroformylation of usually unreactive alkyl acrylates [9].

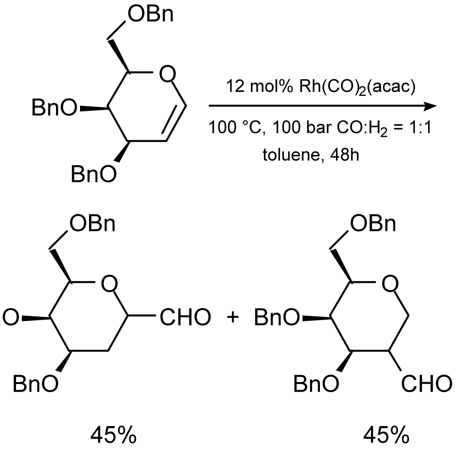
The effects of ligands and pressures in hydroformylation of 1-hexene catalyzed with rhodium fluorinated phosphine complexes in supercritical carbon dioxide and in conventional organic solvents were investigated. The catalytic activities in supercritical carbon dioxide were found to be comparable with those in toluene [10].

Hydroformylation of α,ω-epoxyalkenes using cobalt, rhodium or platinum carbonyl complexes as catalyst precursors was investigated. Practically regiospecific formation of the linear epoxy aldehyde was found at 40 °C and 20 bar ($CO/H_2 = 1/1$) using the catalytic system $RhH(CO)(PPh_3)_3$/XANTPHOS [1].

Tandem enantioselective hydrogenation of prochiral dien amide esters followed by a hydroformylation-cyclization sequence leading to cyclic α-amino acids with ee's >95% was achieved in a single pot, one catalyst system using Rh(I)-Et-DuPHOS [11].

Computation has been used to explore the thermodynamics of isomers and conformers for intermediates along the reaction pathway of the rhodium/XANTPHOS-catalyzed propene hydroformylation. In agreement with experimental results, the computations yield a mixture of diequatorial and axial isomers of $RhH(XANTPHOS)(CO)_2$ as the catalyst resting state. Dissociation of CO from these complexes is computed to be barrierless leading to a computed free energy for exchange of CO ligands around 15 kcal mol^{-1}, somewhat lower than the value of ca. 20 kcal mol^{-1} derived from experimental data. The computed ratios of rates of propene insertion to form n-propyl and i-propyl rhodium-alkyl (42:1) was found to be in good agreement with experimental ratios of n-nonanal to i-nonanal (52:1) for 1-octene hydroformylation [12].

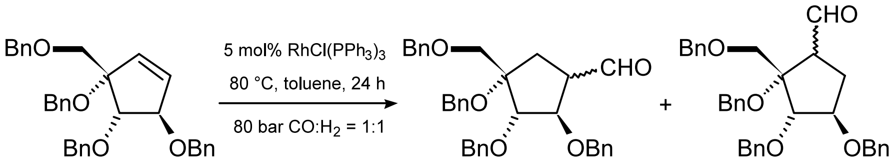
The rhodium-catalyzed hydroformylation reaction of glucals and galactal was investigated. For glucals, the C-2 formyl pyran was the major product whilst for galactal an equimolar mixture of the C-2 and C-1 regioisomers was observed [13]. For example:



Hydroformylation of **5** at 80 °C and 80 bar $CO:H_2 = 1:1$ pressure using 5 mol.% $RhCl(PPh_3)_3$ as the catalyst precursor was found to give an isomeric mixture of **6** and **7** quantitatively [14].

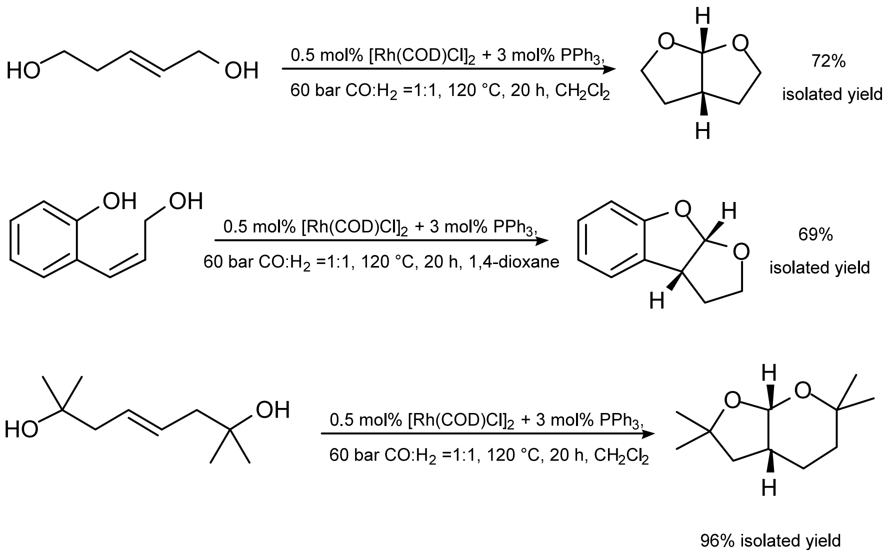
Hydroformylation of 1-hexene using a cationic rhodium complex as the catalyst obtained from $[Rh(COD)]ClO_4$ and 2-(diphenylphosphino)benzaldehyde resulted in 98% yield of aldehydes ($n/iso = 2.6$) [15].

The cationic rhodium A-frame complex $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)_2]^+$ was found to be an active hydroformylation catalyst for styrene at 150 °C and 10 bar $H_2:CO = 1:1$. In addition to the expected aldehydes linear and cyclic ketones are produced in up to 56.5% yield using THF as the solvent and BPh_4^- as the counteranion [16].



5 **6** **7**

A new method for the construction of aliphatic and benzoannulated furo[2,3*b*]furans and furo[2,3*b*]pyrans from α,ω-alkenediols by rhodium-catalyzed tandem hydroformylation/acetalyzation reaction was found [17]. For example:



Triphenylphosphine derivatives modified with thiomethyl and methoxy groups in *ortho*- and *para*-positions of the phenyl ring(s) were tested in the rhodium-catalyzed hydroformylation of 1-hexene. The conversion and the total aldehyde selectivity was found to decrease as a function of cone angle and degree of substitution of the ligand [18].

The (*R*,*R*)- and (*S*,*S*)-1,1′-ferrocenylene-bridged bis-1-phosphanorbornadienes were tested as ligands among others in rhodium-catalyzed asymmetric hydroformylation of styrene. At 50 °C and 20 bar $CO:H_2 = 1:1$ pressure 100% conversion into aldehydes (*iso*/normal = 89/11) was achieved with 15% ee [19].

The addition of even a small amounts of PPh_3 to the dirhodium tetraphosphine hydroformylation catalyst generated from [*rac*-$Rh_2(NBD)_2(Et_2CH_2{-}CH_2(Ph){-}PCH_2P(Ph)CH_2CH_2PEt_2)](BF_4)_2$ was found to cause a drop in the aldehyde linear to branched regioselectivity from 25:1 to 3:1 in 1-hexene hydroformylation in acetone solvent at 90 °C and 6.1 bar $CO:H_2 = 1:1$ pressure [20].

The effect of phosphine and diphosphine ligands on the chemo- and regioselectivity of the rhodium-catalyzed hydroformylation reaction of allylbenzenes and propenylbenzenes was studied. It was found that the rhodium-NAPHOS system promotes the hydroformylation of allylbenzenes into linear aldehydes in near 95% selectivity and propenylbenzenes into branched aldehydes with a formyl group in β-position to the phenyl ring in near 90% selectivity, while the rhodium-dppp system gives branched aldehydes with a formyl group in α-position in near 70% selectivity starting from allylbenzenes [21].

Diphenylphosphine functionalized polyhedral oligomeric silsesquioxane dendrimers were used as ligands for the rhodium-catalyzed hydroformylation of 1-octene. High regioselectivity to the linear nonanal (linear:branched ratio = 14:1) was observed with only one structure within the 1st and 2nd generation dendrimer having a spacer of five atoms between the phosphorus atoms, and carbon–silicon linkage. Lower selectivities were obtained using dendrimers having spacers of three or seven atoms between the phosphorus atoms, and carbon–silicon linkage [22].

Dendrimers with up to 48 phosphine groups were used as ligands in the rhodium-catalyzed hydroformylation of 1-octene. Using dendrimers having diphenylphosphino end-groups, aldehyde products with high linear:branched ratios (12–14/1) were obtained at 120 °C and 10 bar $CO/H_2 = 1$ [23]. Linear to branched ratios up to 3:1 for the alcohol products were obtained by using diethylphosphine dendrimers in the rhodium-catalyzed hydroformylation reaction of 1-alkenes [24].

Rhodium complexes with core-functionalized dendrimeric phosphine ligands were tested as catalysts in both hydroformylation and hydrogenation of alkenes. Generally similar activities were obtained for the dendrimeric systems and the present compounds except in the hydroformylation of a bulky substrate, 4,4,4-triphenyl-1-butene, which gave a significant decrease in activity when the dendrimers were used [25].

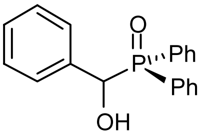
Calixarene phosphites were tested as catalyst components in the rhodium-catalyzed 1-octene hydroformylation reaction at 80 °C and 15 bar $CO:H_2 = 1:1$ pressure. The observed reaction rates lie in the range reported for other medium-bulky phosphites [26].

Rhodium systems with diphosphites built on a cyclodextrin scaffold were found to be effective in catalytic hydroformylation of 1-octene. Turnover frequencies up to 1200 h^{-1} were observed at 80 °C and 20 bar $CO:H_2 = 1:1$ pressure [27].

The rhodium-catalyzed hydroformylation reaction of 1-octene was tested in the presence of new calix[4]arene-based bisphosphonites, bis-phosphites and bis-*O*-acyl-phosphites. Average yields of 80% and *n*/*iso*-ratios of about 1.3–1.5 were observed [28].

The hydroformylation of vegetable oils using $Rh(CO)_2(acac)$ as the catalyst precursor in the presence of PPh_3 or $(PhO)_3P$ was studied [29].

The novel phosphine oxide ligand **1** has been used as a ligand in the rhodium-catalyzed hydroformylation of alkenes with good conversions and regioselectivities. For example the hydroformylation reaction of styrene at 40 °C and 41 bar $CO:H_2 = 1:1$ using 0.6 mol.% $[Rh(CO)_2Cl]_2$ and 1.2 mol.% **1** in chloroform gave 77% conversion in 20 h into 96/4 = branched/linear aldehydes. Using partially resolved ligand 1 (15% ee) in the catalytic hydroformylation of styrene resulted in 25% ee of the branched aldehyde [30].



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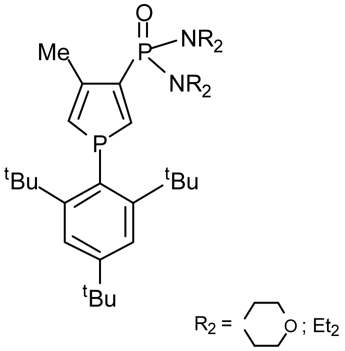
The phosphinated phospholes **9**, **10**, and **11** were tested as ligands in the rhodium-catalyzed hydroformylation of styrene. Higher than 99% chemoselectivity for aldehyde formation with moderate regioselectivities (57–80%) for the branched isomer was observed at 100 °C and 100 bar $CO:H_2 = 1:1$ [31].



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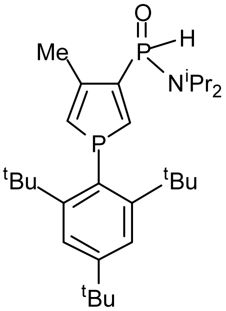

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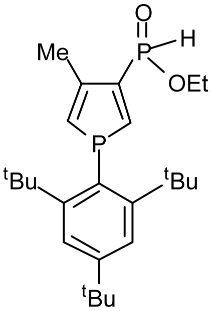
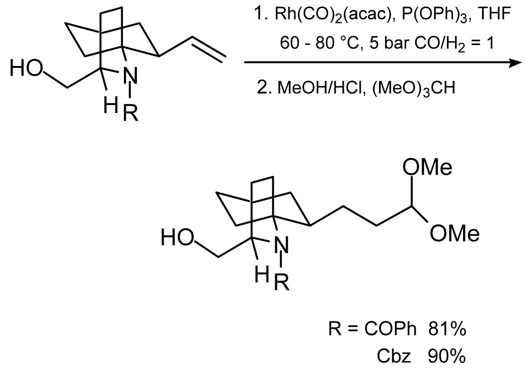


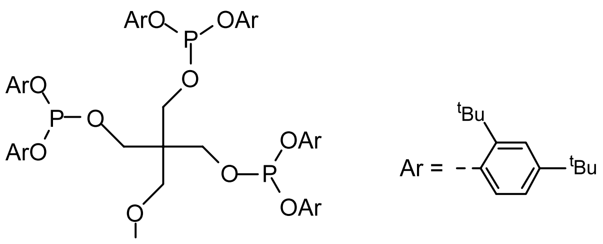
11

Polyether phosphites with over 19 ethylene glycol units were used as ligands in the rhodium-catalyzed non-aqueous hydroformylation of 1-decene. The catalysts were recovered by precipitation from the reaction mixture after reaction on cooling to room temperature or lower. The precipitated catalysts could be reused up to six times without decrease in activity. In situ formed polyetherphosphite/$Ru_3(CO)_{12}$ catalyst was found to be active in hydroformylation of 1-decene in *n*-heptane solution at 130 °C and 50 bar $CO/H_2 = 1$ [32]. The hydroformylation of 1-decene using rhodium complexes of nonionic tension-active phosphine ligands $P[4\text{-}C_6H_4O(CH_2CH_2O)_nH]_3$ in toluene was investigated. At 130 °C and 60 bar $CO:H_2 = 1:1$ the conversion of 1-decene and the yield of aldehyde were found to be 98.6 and 96.0%, respectively. The catalyst has a low solubility at room temperature in toluene, and after separation it can be reused [33]. Under similar reaction conditions the hydroformylation of cyclohexene resulted in a 98.4% yield of cyclohexane carbaldehyde. The thermoregulated phase-separable rhodium catalyst was reused four times and no loss in activity has been found [34]. A thermoregulated phase-separable catalyst formed in situ from $P[4\text{-}C_6H_4O(CH_2CH_2O)_{10}H]_3$ and $RhCl_3 \cdot 3H_2O$ was used in the hydroformylation of diisobutylene. Under the optimum conditions 93.1% conversion of diisobutylene and 82.5% yield of aldehydes were observed. The catalyst could be efficiently recycled up to three times without loss of activity [35].

In the total synthesis of the tricyclic marine alkaloid lepadiformine the hydroformylation reaction using $Rh(CO)_2(acac)/P(OPh)_3$ catalyst precursor was used in one of the steps [36]:

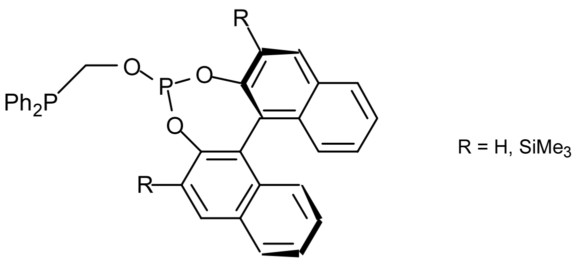


The naturally occurring cinchona alkaloids, cinchonidine, quinine, and quinidine were hydroformylated selectively to the corresponding terminal aldehyde derivatives with 87, 71, and 85% isolated yields, respectively, using $Rh(CO)_2(acac)$/tetraphosphite **12** catalyst system at 90 °C and 20 bar $CO:H_2 = 1:1$ in toluene [37].



12

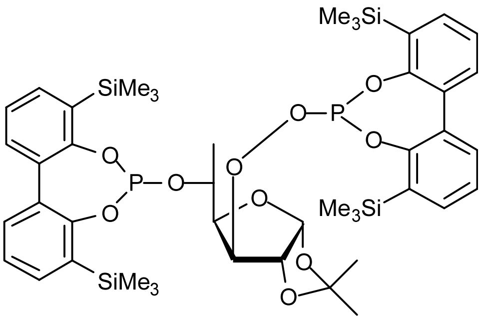
The rhodium-catalyzed hydroformylation of styrene was tested in the presence of the ligand **13**. Using the ligand **13** with $R = SiMe_3$ at 40 °C and 100 bar CO/$H_2 = 1$ 99.9% chemoselectivity for aldehydes with a branched/linear ratio of 32.3 and a 20% ee of the branched aldehyde in the (*S*)-form was obtained. No influence of the ligand/Rh ratio on the enantioselectivity was found [38].



13

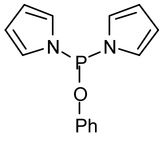
A new series of chiral furanoside phosphite–phosphoramidites [39] and phosphine–phosphites [40] has been screened as ligands in the rhodium-catalyzed asymmetric hydroformylation of styrene. High regioselectivities (up to 97% 2-phenyl-propanal) but only moderate enantioselectivities (up to 65% ee) were found.

By systematic variation in chirality at both chiral sugar backbone stereocenters (C–3 and C–5) and either the axial chiral biphenyl or binaphthyl substituents, both regio- and enantio-selectivities were optimized. Thus, high enantioselectivity (up to 93% *S*) and regioselectivity in 2-phenyl-propanal (up to 98.8%) were found under mild reaction conditions (15–40 °C, 10 bar CO/$H_2 = 1$) for the ligand **14** with a glucofuranoside backbone and trimethylsilyl)-2,2′-biphenyl moiety [41].



14

The influence of properties of ligands **15**, **16**, **17**, and **18** on the catalyst performance in the rhodium-catalyzed hydroformylation and deuterioformylation of 1-octene and 1-hexene, respectively, has been investigated. The pyrrolyl substituents were found to result in a very active catalyst for the hydroformylation of 1-octene. Especially the bidentate pyrrolyl-containing ligand **17** forms a catalyst that shows high activity together with a high regioselectivity for the linear aldehyde and moderate amount of 2-octenes. In the deuterioformylation of 1-hexene using the ligand **17** it was found that the hydride migration is a reversible step under the conditions studied (80 °C, [Rh] = 0.2 mM, $P(CO) = P(D_2) = 10$ bar, [1-hexene] = 0.81 M, in benzene) for both linear and branched alkylrhodium species [42].



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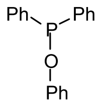

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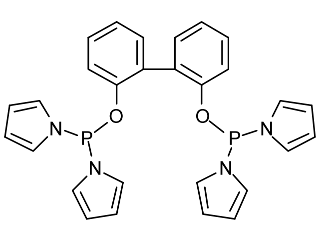

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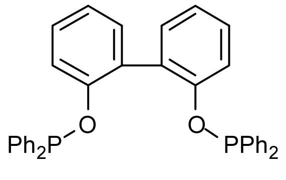
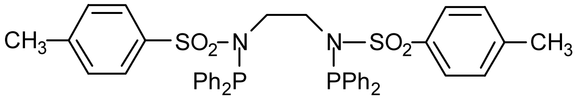


18

The rhodium-catalyzed hydroformylation of 1-hexene was examined in the presence of members of a new class of electron-withdrawing phosphorus ligands, the *N*-sulfonyl-phosphoramides. The chelating compound **19** was found to be the most effective ligand, giving high turnover frequencies and linear to branched ratios of the aldehyde product. For example at a 1000:10:1 ratio of 1-hexene:19:$Rh(CO)_2(acac)$ at 60 °C and 5.8 bar $CO:H_2 = 1:1$ in THF gave 440 mol aldehyde mol^{-1} Rh/h and a normal:*iso* ratio of 10 [43].



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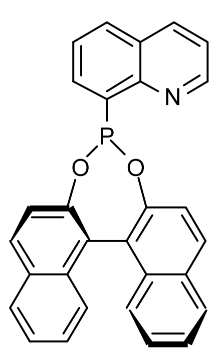
The new ligands **20** and **21** were tested in the rhodium-catalyzed asymmetric hydroformylation of styrene. No asymmetric induction was found even in the presence of an excess of free ligand [44].



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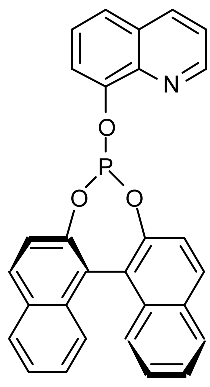
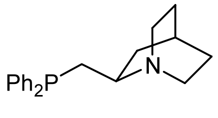


21

New P,N-ligands (**22**, **23**, **24**, and **25**) with a chiral nitrogen center were tested among others in the asymmetric hydroformylation of styrene. At 40 °C and 40 bar $CO:H_2 = 1:1$ about 90/10 branched/linear aldehyde ratios and none or very low ee's were observed [45].

The recyclability of the hydroformylation catalysts employing rhodium(I) and the amphiphilic ligand {4-[bis(2-diethylaminoethyl)aminomethyl]diphenyl}-phosphine was improved by using HCl in the aqueous extraction and subsequent anion metathesis with $NaBPh_4$ [46].

New diaminophosphines **26** and **29** were tested as ligands in the rhodium-catalyzed hydroformylation of styrene and compared to that of the aminophosphines **27** and **28**. The observed trends were found to be related to the basicity of the dangling amine function and to its proximity to the metal center [47].



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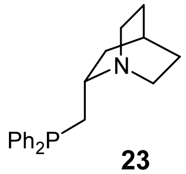

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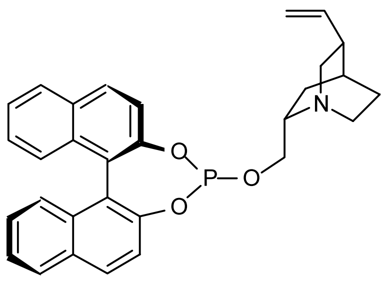

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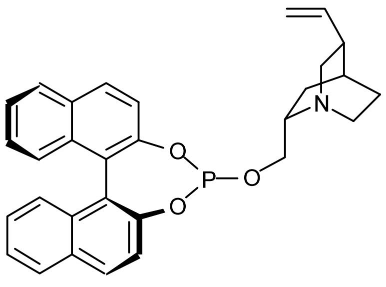

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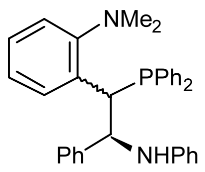

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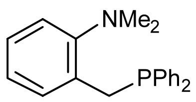

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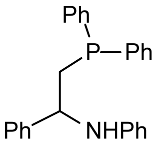

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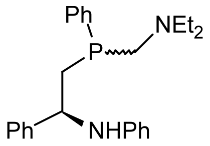


29

The rhodium-catalyzed asymmetric hydroformylation of vinylarenes with chiral P,N-ligands based on the DIOP skeleton was investigated. The systems were found to be active at mild conditions (25 °C and 5 bar $CO/H_2 = 1$) leading to a maximum of 23% ee of the branched aldehyde [48].

See also Refs. [1,51,57,59,60,67,69,70,115].

1.1.3. Other metals as catalysts and bimetallic catalysts

The homogeneous catalytic hydroformylation of ethylene in supercritical carbon dioxide was studied using $Ru_3(CO)_{12}$ as the catalyst precursor in the temperature range between 60 and 125 °C and in the pressure range from 224 to 408 bar [49].

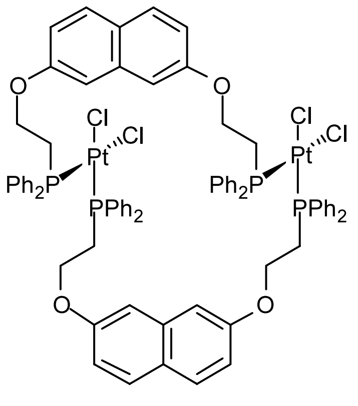
Catalyst systems consisting of a palladium(II) diphosphine complex with weakly or non-coordinating counterions were found to be efficient catalysts for the hydrocarbonylation of higher olefins. Variation of ligand, anion and/or solvent were used to steer the reaction selectively towards aldehydes/alcohols, ketones or oligoketones. Non-coordinating anions and arylphosphine ligands were found to produce primarily (oligo)ketones, while increasing ligand basicity shifts selectivity towards monoketones. Increasing ligand basicity and/or increasing anion coordination strength leads to high selectivity for hydroformylation products, aldehydes and alcohols [50].

Dithiolato-bridged heterobimetallic MRh (M = Pt, Pd) complexes were tested as catalyst precursors in the hydroformylation of styrene. High pressure in situ NMR studies showed that mononuclear species are formed under catalytic conditions. Comparisons of the catalytic activities with that of a related cationic mononuclear rhodium complex showed that there is no particular advantage using the heterobimetallic precursors [51].

Hydroformylation of 1-octene using the platinum stanna-closo-dodecaborate complexes, $[(dppp)PtPh(SnB_{11}H_{11})]^-$ and $[(dppp)Pt(SnB_{11}H_{11})_2]^{2-}$ (dppp = $Ph_2PCH_2CH_2CH_2PPh_2$) as the catalyst was studied [52].

The isolated 'preformed' platinum catalyst $[Pt(PP_3)(SnCl_3)]SnCl_3$ (PP_3 = tris[2-(diphenylphosphino)ethyl]-phosphine from the precursor $[Pt(PP_3)Cl]Cl$ and $SnCl_2$ was found to show high aldehyde selectivity (99%) in styrene hydroformylation at 100 °C and 100 bar $CO/H_2 = 1$ [53].

The metallamacrocycle **30** combined with two equivalents of $SnCl_2$ was tested as catalyst in 1-octene hydroformylation. At 60 °C and 40 bar $CO/H_2 = 1$, complete conversion to nonanal (87%) and 2-methyloctanal (11%) was found [54].



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The hydroformylation of camphene in the presence of $PtCl_2L_2/SnCl_2/PPh_3$ or $PtCl_2(PhCN)_2/SnCl_2$/diphosphine catalytic systems ($L_2 = 2PPh_3$, dppe, dppp, dppb, diphosphine = BINAP, DIOP) was studied. The highest diastereomeric excess (60%) is achieved with the platinum/tin/(*R*)- or (*S*)-BINAP system which shows ca. 85% chemoselectivity for the linear aldehydes at ca. 90% camphene conversion [55].

Parahydrogen-induced polarization in NMR spectra of the heptanal product was observed in hydroformylation of 1-hexene using *cis*-$PtCl_2(CO)(PPh_3)$—$SnCl_2$ as the catalyst. The observed formyl proton polarization indicates a parahydrogen origin [56].

See also Refs. [1,32].

1.2. Heterogeneous systems

1.2.1. Supported complexes

Three-dimensional entrapment of the chiral rhodium cationic complex prepared from (*R*)-(+)-2,2′-bis(diphenylphosphino)-4,4′-bisphosphono-1,1′-binaphthyl and $[Rh(OMe)(COD)]_2$ by electrostatic attraction between a polyelectrolyte and the oppositely charged rhodium complex was tested as heterogenized catalyst in enantioselective hydroformylation of styrene and vinyl acetate. An enantiomeric excess of 39% was achieved in the hydroformylation of vinyl acetate, which is comparable to results obtained in aqueous biphasic hydroformylation or in the same order as obtained with homogeneous Rh-BINAP catalysts [57].

Apatitic tricalcium phosphate was used as support for supported aqueous phase hydroformylation of 1-octene at 80 °C in toluene using a dinuclear rhodium complex bearing TPPTS as hydrophilic ligands. The high aldehyde yield observed with the apatitic tricalcium phosphate was attributed to the favorable orientation of the catalytic molecule arising from the absorption of some of the TPPTS ligands onto the hydrophilic surface of apatite [58].

Hydroformylation of 1-hexene in supercritical carbon dioxide was investigated using a rhodium-phosphine catalyst tethered to a silica support. The performance of the tethered catalyst was compared with a homogeneous rhodium–phosphine catalyst, and was found to be equally effective under identical reaction conditions [59].

A rhodium thiolate complex with 4,6-dimethyl-2-mercaptopyrimidine tethered to chemically modified silica was tested as a catalyst in the hydroformylation reaction of 1-heptene. The heterogenized catalyst was found to be active even in the absence of PPh_3 in the reaction medium and could be reused in several cycles [60].

Correlation of structure and propene-hydroformylation performance of $RhH(CO)[P(m\text{-}C_6H_4SO_3Na)_3]_3$ supported on SiO_2 was investigated [61].

Polysiloxane-bound rhodium(I) phosphine complexes were tested in the hydroformylation of 1-hexene at 70 °C and 60 bar $CO{:}H_2 = 1{:}1$ using a catalyst:substrate ration of 1:16 000 in toluene or dichloromethane. Up to 891 mol aldehyde mol^{-1} catalyst/h with a 0.53 $n/(n+iso)$ aldehyde ratio and no leaching of the rhodium was reported [62].

Supported ionic liquid catalysis—a new concept for hydroformylation catalysis—have been described and useded for 1-hexene hydroformylation [63].

Amphiphilic resin-supported rhodium–phosphine complexes on polystyrene-poly(ethylene glycol) graft co-polymer (1% divinylbenzene cross-linked) beads were found to exhibit high catalytic activity in water to promote among others the hydroformylation reaction of 1-alkenes [64].

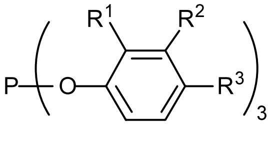
See also Ref. [6].

1.2.2. Biphasic systems

Improved selectivity, catalyst retention and product separation were reported in the hydroformylation of linear terminal alkenes using rhodium based catalysts under fluorous biphasic conditions. The best results, which compare well with those obtained in commercial systems were obtained using Rh (2.0 mmol dm^{-3})/$P(4\text{-}C_6H_4C_6F_{13})_3$ (20 mmol dm^{-3}) at 70 °C and 20 bar CO/H_2 to give a linear aldehyde selectivity of 80.9% and an initial productivity of 8.8 mol dm^{-3} h^{-1}. Rhodium leaching into the aldehyde phase was found to be 0.05% of the rhodium charged, and the phosphorus leaching is 3.3% [65].

Effects of fluorinated groups on the activity and selectivity of the biphasic hydroformylation catalytic system with rhodium/tris-((1*H*,1*H*,2*H*,2*H*-perfluorodecyl)phenyl)phosphites complexes were investigated. The activities and the selectivities were found to vary markedly with the position of the perfluoroalkylgroup on the aromatic ring [66].

The hydroformylation of 1-alkenes (1-hexene, 1-octene, and 1-decene) and internal alkenes (2-octene, 4-octene, and cyclohexene) were studied in the presence of fluorous-soluble triphenylphosphite derivatives (**31**)-modified rhodium catalyst at 80 °C and 40 bar $CO{:}H_2 = 1{:}1$ pressure in an olefin/$C_8F_{17}H$ solvent mixture that forms a homogeneous liquid phase at the reaction temperature but separates at room temperature. Activities up to 10 000 h^{-1} and normal to branched aldehyde ratios up to 5.8 = normal/*iso* were obtained in the case of 1-decene hydroformylation [67].



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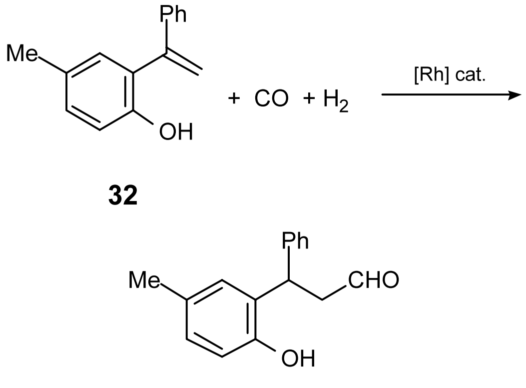
$R^1 = C_8F_{17}$, R^2, $R^3 = H$
R^1, $R^3 = H$, $R^2 = C_8F_{17}$
R^1, $R^2 = H$, $R^3 = C_8F_{17}$
$R^1 = CH_3$, $R^2 = H$, $R^3 = C_8F_{17}$
R^1, $R^3 = C_8F_{17}$, $R^2 = H$
$R^1 = C_8F_{17}$, $R^2 = H$, $R^3 = COC_7F_{15}$

A new inverted biphasic catalysis system using supercritical CO_2 as the stationary catalyst phase and water as the continuous phase was described for rhodium-catalyzed hydroformylation of polar substrates. Product separation and catalyst recycling was possible without depressurising the autoclave. Turnover numbers of up to 3560 were obtained in three consecutive runs and rhodium leaching into the aqueous phase was below 0.3 ppm [68].

Triaryl-phosphines and -phosphites bearing fluorous ponytails combined with $Rh(CO)_2(acac)$ in perfluoro-1,3-dimethyl-cyclohexane were found to give high rates, good linear selectivity and good retention of catalyst in the fluorous phase during hydroformylation of 1-octene [69].

The hydroformylation of **32** catalyzed by rhodium complexes both in homogeneous or in aqueous biphasic system was found to afford the linear aldehyde **33** in about 80–90% yield [70].



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The water-soluble complex derived from $Rh(CO)_2$(acac) and human serum albumin was found to be efficient in the hydroformylation of styrene and 1-octene at 60 °C and 70 bar $CO/H_2 = 1$ even at very low catalyst concentrations [71].

The effects of Na_2SO_4 on the reaction rate of the biphasic hydroformylation of 1-hexene using the $RhCl(CO)(TPPTS)_2$—TPPTS—CTAB catalyst system were investigated at 90 °C and 15 bar $CO:H_2 = 1:1$. The optimal $[Na_2SO_4]/[Rh]$ value was found to be dependent on the applied [Rh]/[TPPTS] ratios [72].

The biphasic rhodium-catalyzed hydroformylation of propylene using 1-phenyldibenzophosphole disulfonate was studied. At 100 °C, 20 bar $CO:H_2 = 1:1$, ligand:Rh = 35, agitating speed = 500 r min^{-1}, rhodium concentration = 3.6×10^{-8} mol l^{-1}, a turnover number of 2800 g (butyraldehyde)/g(Rh) h and a normal/*iso* ratio of 12.3 was obtained. Compared with the performance of TPPTS under the same condition, both activity and selectivity are better with 1-phenyldibenzophosphole disulfonate [73].

The kinetics of hydroformylation of propylene using water-soluble $RhCl(CO)(TPPTS)_2$/TPPTS catalyst was studied. The activation energy was found to be in the range of 75–85 kJ mol^{-1} [74]. The kinetics of biphasic hydroformylation of 1-dodecene catalyzed by the water-soluble catalyst $RhCl(CO)(TPPTS)_2$ has been investigated in the presence of cetyltrimethylammonium bromide at pressures from 9 to 13 bar and temperatures from 80 to 100 °C [75].

Hydroformylation of 1-dodecene using a rhodium-TPPTS catalyst in a microemulsion has been described. High activities and good selectivities towards the *n*-aldehyde were achieved at 80 °C and 80 bar $CO:H_2 = 1:1$. The reaction rates were found to be higher than those in a two-phase system [76]. Hydroformylation of 7-tetradecene using rhodium-TPPTS catalyst in a microemulsion system stabilized by technical grade surfactants of the alkyl-polyglycolether type gave 2-hexylnonanal selectively at 120 °C and 100 bar $CO:H_2 = 1:1$ pressure [77].

The state of the art of aqueous biphasic catalysis has been disclosed in connection with the Ruhrchemie/Rhône-Poulenc oxo process [78].

The addition of di(*m*-sulfophenyl)phenylphosphine into the biphasic catalytic system containing $RhCl(CO)(TPPTS)_2$—TPPTS—CTAB was found to increase the regioselectivity. The ratio of linear/branched aldehyde in 1-dodecene hydroformylation at 100 °C and 15 bar CO/H_2 rise from 6.5 (without TPPDS) to 22.3 ([TPPTS]/[TPPDS] = 2:1) [79].

The turnover frequency in the hydroformylation of 1-hexene in the biphasic system with $RhCl(CO)(TPPTS)_2$, TPPTS and cetyltrimethylammonium bromide was found to be decreased by the addition of salts in the order $M^{3+} > M^{2+} > M^{+}$ [80].

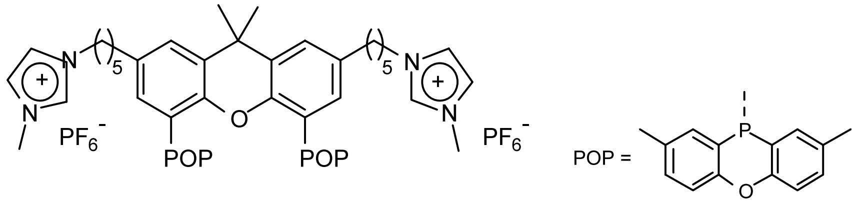
The effect of reaction engineering factors on the biphasic hydroformylation of 1-dodecene catalyzed by the water-soluble rhodium complex $RhCl(CO)(TPPTS)_2$ was investigated at 100 °C and 11 bar $CO/H_2 = 1/1$. High agitation intensity was found to be beneficial for olefin conversion and reaction rate, but adversely affected the normal/*iso* aldehyde ratio [81].

Nonionic water-soluble phosphines $P[4\text{-}C_6H_4(OCH_2CH_2)_nOH]_3$ ($N = 3n = 18, 25$) and $Ph_2P[4\text{-}C_6H_4(OCH_2CH_2)_nOH]$ ($N = 3 = 18, 25$) combined with $Rh(CO)_2$(acac) have been used for the hydroformylation of higher olefins at 100 °C and 50 bar $CO/H_2 = 1$. An average turnover frequency of 182 h^{-1} for 1-hexene was observed. The inverse temperature-dependent water solubility of the phosphines allows recovery and reuse of the catalyst [82].

The newly synthesized ionic compounds 1,2,3-trimethylimidazolium triflate and 1-ethyl-2,3-dimethylimidazolium triflate and the coordination compound (3-butylimidazole)triphenylboron were used as solvents for biphasic rhodium-catalyzed hydroformylation of 1-hexene and 1-dodecene. High conversions with varying liner/branched aldehyde ratios were observed. In comparison to the conventional solvent toluene, similar turnover numbers but a higher tendency towards isomerization and hydrogenation was found [83].

A novel phenoxaphosphino-modified ligand **34** was used as a ligand in the rhodium-catalyzed hydroformylation of 1-octene in ionic liquids. Very high linear selectivity and high activity were found with complete retention of the catalyst in the ionic phase [84].

See also Refs. [32,35,37,46,81].



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1.3. Coordination chemistry related to hydroformylation

The migratory insertion of a methyl group into a Co–CO bond of $CH_3Co(CO)_4$ and the coordination of CO to $CH_3C(O)Co(CO)_3$ were studied using gradient-corrected density functional theory techniques. Two stable 16-electron acyl intermediates have been located on the B3LYP potential energy surface, which have the carbons of the acyl groups in the axial position. One of them is stabilized by the formation of an agostic interaction to the vacant site of the trigonal bipyramid, and the other is stabilized by the acyl oxygen adapting an η^2-coordination geometry. The calculations indicate that the reaction of the intermediates is probably competitive [85].

The migratory insertion reaction of carbon monoxide into cobalt-alkyl and manganese-alkyl bonds were studied by the time-resolved infrared and time-resolved optical detection of reactive intermediates generated by laser flash photolysis of suitable organometallic precursors [86].

The homogeneous rhodium-catalyzed hydroformylation of 3,3-dimethyl-1-butene in *n*-hexane was studied at 25 °C and variable total pressure using high pressure in situ infrared spectroscopy as the analytical tool. All anticipated major and minor component spectra were reconstructed using band-target entropy minimization without spectral preconditioning. Beside $Rh_4(\sigma\text{-}CO)_9(\mu\text{-}CO)_3$, $RC(O)Rh(CO)_4$ and $Rh_6(CO)_{16}$ the presence of a previously unknown complex $Rh_4(\sigma\text{-}CO)_{12}$ was identified [87]. The same technique has led to the reconstruction of the pure component spectra of $RhH(CO)_4$ and $RhD(CO)_4$ for the first time [88].

Results of investigations of reactions of $RhH(CO)L_3$ ($L = P(3,5\text{-}(CF_3)_2C_6H_3)_3$) with CO, H_2 and ethylene in supercritical CO_2 solutions using a high temperature high-pressure transmission FTIR probe have been reported. The rhodium complex $RhH(CO)L_3$ was found not to dissociate in $scCO_2$. It is converted to $RhH(CO)_2L_2$ and to $[Rh(CO)_2L_2]_2$ in the presence of CO and mainly to $RhH(CO)L_2$ in the presence of an equimolar mixture of CO and H_2. In the presence of CO and C_2H_4, three different acylrhodium complexes, $EtC(O)Rh(CO)L_2$, $EtC(O)Rh(CO)_2L$, and $EtC(O)Rh(CO)_3L$ were found in the solution. Similar species have also been observed during the hydroformylation reaction [89].

A quantum mechanics/molecular mechanics study of the steric influence of the PR_3 spectator ligands on the energetics of ethylene insertion into the Rh–H bond of $RhH(PR_3)_2(CO)(\eta^2\text{-}CH_2{=}CH_2)$ has been made ($R =$ Me, ^{t}Bu, Ph, $3\text{-}C_6H_4SO_3^-$, $4\text{-}C_6H_4SO_3^-$). The calculations predict that two reaction channels, one originating from the more stable mixed equatorial, axial arrangement and the other from the less stable bis-equatorial arrangement of the two PR_3 ligands, will be operative for the ethylene insertion with the PMe_3 ligand system. The latter will be preferred thermodynamically over the former. In the case of the aryl phosphine ligands, a clear energetic preference, kinetically and thermodynamically, was found for ethylene insertion to proceed from the least stable bis-equatorial ethylene adduct versus the paths originating from the more stable equatorial, axial ethylene adduct [90].

The structure and reactivity of the anionic complexes $[M(CO)_2I_2]^-$ ($M = Rh$, Ir), supported on ion exchange resins were investigated. Infrared spectroscopy and extended X-ray absorption fine structure measurements have shown that the supported complexes adopt square planar structures similar to those found in solution. The kinetics of the oxidative addition of MeI with the polymer-supported complexes have also been studied [91].

See also Refs. [2,12].

1.4. Engineering aspects of hydroformylation

The potential of carbon dioxide in its liquid or supercritical state as an environmentally benign reaction medium for sustainable chemical synthesis such as olefin hydroformylation has been discussed [92].

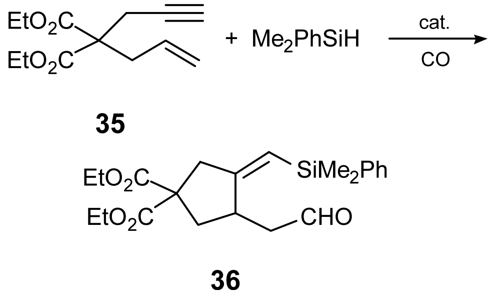
See also Refs. [35,81].

2. Hydroformylation related reactions of CO

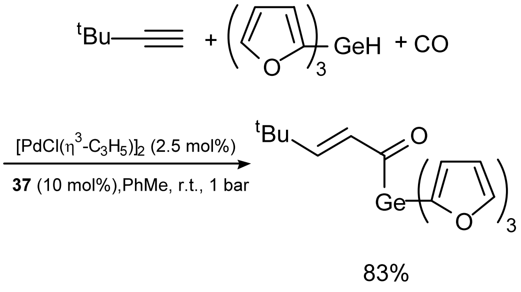
2.1. Silylformylation, silylcarbocyclization, and hydrogermylcarbonylation

Rhodium-catalyzed silylformylation has been applied in a highly efficient synthesis of polyketides by tandem intramolecular silylformylation–crotylsilylation [93].

The rhodium-catalyzed (0.5 mol.% $Rh_4(CO)_{12}$ and 10 mol.% $P(OEt)_3$) carbonylative silylcarbocyclization reaction of 1,6-enynes such as **35** at 105 °C and 20 bar of CO in 1,4-dioxane was found to afford **36** as essentially the sole product in 91% isolated yield [94].

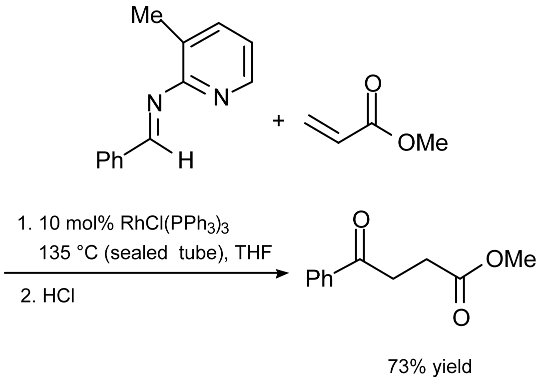


The palladium–phosphite complex from $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and $(2,5\text{-di-}^t BuC_6H_3O)_3P$ (**37**) was found to catalyze efficiently the reaction of alkynes with tri(2-furyl)germane providing α,β-unsaturated acylgermanes under ambient carbon monoxide pressure [95]. For example:



2.2. Hydroacylation, hydrocarboxylation, and alkoxycarbonylation

1,4-Dicarbonyl compounds were prepared in up to 98% yield in rhodium-catalyzed hydroacylation reactions between (2-aminopicolyl)imines and acrylate esters followed by acid hydrolysis [96]. For example:



The addition of CO and methanol to 3,3,3-trifluoropropyne was found to be catalyzed by palladium(II) acetate in the presence of (6-methylpyrid-2-yl)diphenylphosphine and methanesulfonic acid. The main products of the reaction are the methyl esters of 2-(trifluoromethyl)propenoic acid and of 4,4,4-trifluorobut-2-enoic acid. The regioselectivity of the reaction can be controlled by a suitable choice of the composition of the catalytic system and the reaction conditions. Thus, the methyl ester of 2-(trifluoromethyl)propenoic acid can be obtained in 93% yield by using $P(CO) = 20$ bar and high ligand/Pd and acid/Pd ratio. On the other hand, selectivity up to 85% in the methyl ester of 4,4,4-trifluorobut-2-enoic acid can be achieved using $P(CO) = 80$ bar and a low ligand/Pd ratio together with a high acid/Pd ratio [97].

Novel heterogeneous catalysts containing a palladium complex anchored on mesoporous supports for hydrocarboxylation of aryl olefins and alcohols were found to give high regioselectivity, activity and recyclability without leaching of palladium complex from the supports. In styrene hydrocarboxylation at 115 °C and 31 bar CO pressure 2-phenyl-propionic acid is formed with 99% selectivity at 2600 mol styrene mol^{-1} palladium h^{-1} turnover frequency [98].

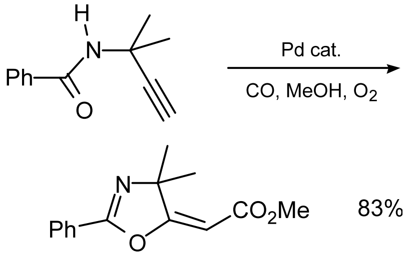
The effect of the reaction conditions on the composition of products in the $PdCl_2(PPh_3)_2/SnCl_2\cdot 2H_2O/PPh_3$-catalyzed methoxycarbonylation of dihydro-myrcenol was studied [99].

High catalytic activity ($TOF = 282\ h^{-1}$) and selectivity to the branched product (~91%) was found in the biphasic hydrocarboxylation of styrene using a novel water-soluble palladium complex, $[Pd(pyridine\text{-}2\text{-}carboxylato)(TPPTS)]^+TsO^-$ as the catalyst [100].

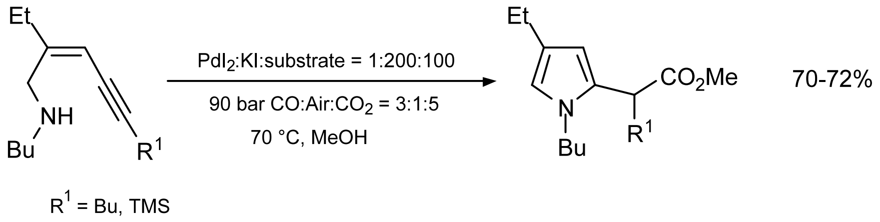
The homogeneous catalytic system $PdCl_2(PPh_3)_2/H_5PMo_{10}V_2O_{40}/HCl/CO/H_2O$ [101], and $PdCl_2(PPh_3)_2/CO/CH_3OH$ [102] in THF was found to be efficient for the regioselective hydrocarboxylation of styrene leading to the branched carboxylic acid (> 99%) at 80 °C and 40 bar CO [101,102].

Pyrimidine-modified palladium(II) complexes were found to catalyze the methoxycarbonylation of styrene to give dimethyl phenylsuccinate as the major product [103].

A variety of prop-2-ynylamides were converted into oxazolines containing the alkoxycarbonyl)methylene moiety in a palladium-catalyzed oxidative cyclization-alkoxycarbonylation process. The reaction was carried out in alcoholic media at 50–70 °C and under 24 bar pressure of 3:1 = CO:air in the presence of catalytic amounts of PdI$_2$ in conjunction with KI [104]. For example:



Carbon dioxide was found to act as a promoter in the palladium-catalyzed oxidative cyclization-alkoxycarbonylation reaction of (*Z*)-(2-en-4-ynyl)amines leading to pyrrol-2-acetic esters. Without using carbon dioxide the reaction is less selective and gives much lower yields [105].

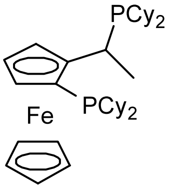


The methoxycarbonylation of 38 at 0 °C and 1 bar CO in the presence of 5 mol.% (MeCN)$_2$PdCl$_2$ and 1.1 equiv. *p*-benzoquinone was found to give the cyclic ketal 39 in 82% yield as a single diastereomer [106].

Mono- and di-nuclear phosphinothiolato complexes of rhodium and iridium were found to be much more effective in catalyzing the carbonylation of methanol to acetic acid than the previously known catalyst [RhI$_2$(CO)$_2$]$^-$ [107].

Effects of the catalyst precursor, triphenylphosphine, base, pressure and reaction temperature on the reaction yield and selectivity in the palladium-catalyzed alkoxycarbonylation of allyl bromide to unsaturated esters in supercritical carbon dioxide was studied. Iron(II) chloride was found to have a promoting effect as a cocatalyst on the reaction [108].

The palladium-catalyzed butoxycarbonylation reaction of activated and deactivated aryl chlorides was examined with regard to the influence of critical reaction parameters, product selectivity, and the performance of various catalyst ligands. In the chlorobenzene carbonylation the PdCl$_2$(PhCN)$_2$/**40** catalyst was found at the optimum 130–145 °C and 1–3 bar CO pressure to be more than one order of magnitude more productive than other known palladium catalysts [109].



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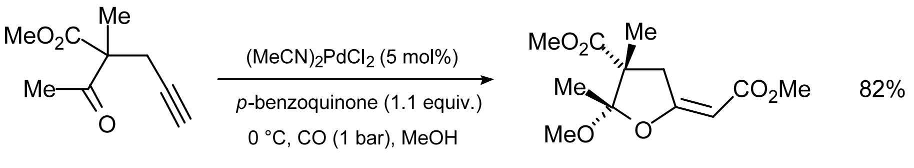
The enol triflate of 3-tropinone was converted into methyl trop-2-ene-3-carboxylate in 65% isolated yield by the palladium-catalyzed methoxycarbonylation using



38 **39**

$Pd(OAc)_2$ and 1,2′-bis(diphenylphosphino)ferrocene as catalyst precursors at room temperature and atmospheric pressure of CO [110].

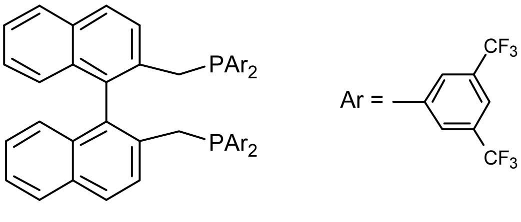
Palladium complexes immobilized onto PAMAM (for the structure of PAMAM see for example: L.J. Twyman, A.S.H. King, I.K. Martin, Chem. Soc. Rev. 31 (2002) p. 78) dendrimers supported on silica were used as catalysts for the carbonylation of iodoarenes in methanol to form the corresponding methyl carboxylates. The catalyst could be recycled four to five times without significant loss of activity [111].

Steric and electronic effects on the reactivity of rhodium and iridium complexes containing P–S, P–P, and P–O ligands in the reaction with methyl iodide have been studied using kinetic methods. The results are discussed in the context of catalytic methanol carbonylation [112].

See also Refs. [115–117].

2.3. Amidocarbonylation and hydroaminomethylation

The selective synthesis of linear amines from internal olefins or olefin mixtures was achieved through a rhodium/phosphine (**41**)-catalyzed one-pot reaction at 120 °C, $P(H_2) = 50$ bar and $P(CO) = 10$ bar, consisting of an initial olefin izomerization followed by hydroformylation and reductive amination [113]. The significance of this atom efficient one-pot rhodium/phosphine-catalyzed synthesis of linear amines from internal olefins has been put in perspective [114].



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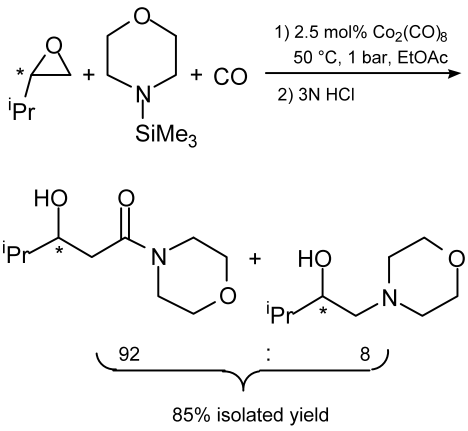
New steroidal derivatives of androstene and pregnene containing an α-amino moiety have been prepared in a one-pot hydroformylation–amidocarbonylation reaction using a rhodium or a rhodium–cobalt complex catalyst [115].

Carbonylation reactions of allene in alcohols and amines in the presence of $Ru_3(CO)_{12}$ precatalyst at 100 °C and 15 bar CO pressure gave methacrylates and methacrylamides, respectively in up to 89% yield with an atom economy of 100% [116].

A mild and efficient carbonylation protocol for the cobalt-catalyzed conversion of optically active epoxides to b-hydroxy morfoline amides has been described [117]. For example:



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

Ruthenium complexes with phenanthroline or bipyridine ligands in aqueous 2-ethoxyethanol in the presence of a base were found to catalyze the water–gas shift reaction at 100 °C and 0.9 bar CO partial pressure [118].

The reaction of $[Ru(dppe)(CO)(H_2)_3][OTf]_2$ with CO in acetone/water was found to give $[Ru(dppe)(CO)_3H][OTf]$ via a water–gas shift reaction [119].

The aqueous/organic two-phase reduction of nitroarenes to the corresponding amines by CO using the thermoregulated phase-transfer catalyst $Ru_3(CO)_9(PEO\text{-}DPPSA)_3$ (PEO-DPPSA = poly(ethylene oxide)-substituted 4-(diphenylphosphino)benzenesulfonamide) was investigated. Good activities and selectivities were observed in nitro group reduction even if halogen, carbonyl or cyano groups were present in the substrates. E.g.: at 140 °C and 40 bar CO pressure using 0.1 mol.% catalyst in 10 h, 97.5% conversion of $2\text{-}ClC_6H_4NO_2$ and $> 99\%$ selectivity in the formation of $2\text{-}ClC_6H_4NH_2$ was observed. The catalyst in the water phase could be recycled three times with only a little loss of catalytic activity [120].

Immobilized $Rh_2(CO)_4Cl_2$ on poly(4-vinylpyridine) was found to be active for the water–gas shift reaction and nitrobenzene reduction to azoxybenzene at 100 °C and 0.9 bar CO in the presence of 80% aqueous 2-ethoxyethanol [121].

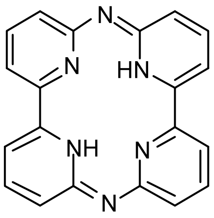
2.5. Reduction of CO and CO_2

The photocatalytic CO_2–CO reduction using [*fac*-$Re(bpy)(CO)_3P(O^iPr)_3]SbF_6$ as the catalyst was investigated at room temperature. In a two-phase system at a CO_2 pressure of 13.6 bar using triethanolamine as an electron donor, the turnover number for CO formation reached a maximum value of 15.6 in 24 h [122].

Different phosphines were tested, in combination with Ru(II) precursors, for their ability to form active catalysts for the hydrogenation of CO_2 to formic acid in the presence of NPr_3 and methanol. The phosphines PMe_3, $PPhMe_2$, dppm, dppe, and *cis*- and *trans*-$Ph_2PCH{=}CHPPh_2$ were found to result in high formic acid yields (over 0.6 mol mol^{-1} of NPr_3 in the first 1 h) at 50 °C, $P(H_2) = 40$ bar and $P(total) = 100$ bar [123].

Turnover frequencies up to 95 000 h^{-1} were observed in catalytic hydrogenation of CO_2 to formic acid using $RuCl(O_2CMe)(PMe_3)_4$ as the precatalyst combined with pentafluorophenol and triethylamine in supercritical CO_2 [124].

Electrocatalytic reduction of carbon dioxide to carbon monoxide and/or formic acid was investigated using cobalt(II), nickel(II) and copper(II) complexes of the hexaazamacrocycle ligands **42** and **43**. The results of cyclic voltametric and UV–vis spectroscopic measurements show that the metal center in its lower oxidation state is the active site [125].



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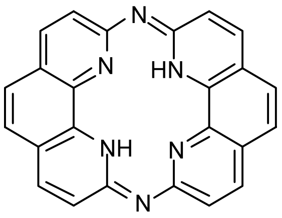

43

3. Reviews

1) Recent advances in rhodium-catalyzed cyclization reactions. A review with 44 references of cyclohydrocarbonylation processes (a combination of hydroformylation and cyclization), which serve for the rapid construction of monocyclic, bicyclic, and fused ring systems from readily obtainable starting materials [126].
2) New cyclization reactions in organic syntheses. A review with 18 references of the transition metal-catalyzed cyclization reactions developed in the author's laboratories, which include among others silylcarbocyclizations, carbonylative carbotricyclizations, intramolecular silylformylations and desymmetrization of siloxydiynes by sequential double silylformylation [127].
3) The production of low molecular weight oxygenates from carbon monoxide and ethene. A review with 70 references [128].
4) Unraveling the bite angle effect—new ligands for selective hydroformylation of internal alkenes. A review with 9 references [129].
5) Role of ligands in homogeneous catalysis based on transition metals. Research related to simulation of biocatalytic processes has been considered with 19 references [130].
6) Phosphorus heterocycles: from laboratory curiosities to ligands in highly efficient catalysts. A review of rhodium catalysts with various phosphabenzenes and phosphaferrocene ligands among others in hydroformylation of terminal and internal alkenes with 48 references [131].
7) XANTPHOS-based, silica-supported, selective, and recyclable hydroformylation catalysts. A review of immobilized catalysts based on xanthene ligands with 49 references [132].
8) Applications of ionic liquids in organic synthesis. A review to summarize some of the recent advances in the application of ionic liquids among others in hydroformylation, with 104 references [133].
9) Continuous catalytic reactions in supercritical fluids. A review on the most recent developments among others in hydroformylation with 84 references [134].
10) Heterogeneous and solid supported dendrimer catalysts. A review of the heterogeneous and solid supported peripherally functionalized dendrimers in catalysis, among others in hydroformylation with 37 references [135].
11) Synthetic applications of palladium catalyzed carbonylation of organic halides. A review with 153 references [136].
12) Multi-electron reduction of CO_2 via $Ru{-}CO_2$, $-C(O)OH$, $-CO$, $-CHO$, and $-CH_2OH$ species. A review of ruthenium model complexes of reaction intermediates in the multi-electron reduction of CO_2 catalyzed by metal complexes with 83 references [137].

Acknowledgements

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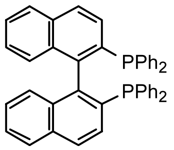
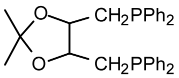
Appendix A: List of abbreviations

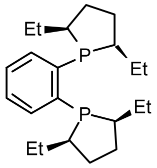
Ac	acetyl
acac	acetylacetonate
Ar	aryl
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl



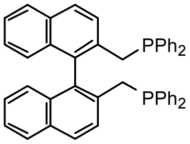
Bn	benzyl
bpy	2,2′-bipyridine
Bu	butyl
Cbz	benzyloxycarbonyl (carbobenzoxy)
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
CTAB	cetyltrimethylammonium bromide
DIOP	2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane



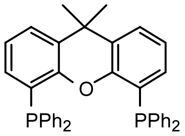
DMF	*N*,*N*-dimethylformamide
dppb	$Ph_2PCH_2CH_2CH_2CH_2PPh_2$
dppe	$Ph_2PCH_2CH_2PPh_2$
dppp	$Ph_2PCH_2CH_2CH_2PPh_2$
ee	enantiomeric excess
Et	ethyl
Et-DuPHOS	



IR	infrared
Me	methyl
NAPHOS	2,2′-bis(diphenylphosphanylmethyl)-1,1′-binaphthyl



NBD	norbornadiene
Ph	phenyl
py	pyridine
sc	supercritical
THF	tetrahydrofuran
Tf	triflate (trifluoroacetyl)
TMS	trimethylsilyl
TOF	turnover frequency (mol product (mol cat)$^{-1}$ time^{-1})
TPPDS	disodium salt of the disulfonated triphenylphosphine
TPPTS	trisodium salt of the trisulfonated triphenylphosphine
Ts	tosyl (*p*-toluenesulfonyl)
TsOH	*p*-toluenesulfonic acid
UV–vis	ultraviolet–visible
XANTPHOS	



Appendix B: The metals and their associated references

Metal	Refs.
V	[102]
Cr	[5]
Mo	[5,102]
W	[5,102]
Mn	[86]
Re	[122]
Fe	[19,108,110]
Ru	[32,49,116,118–120,123,124,137]
Co	[1,2,85,86,115,117,125]
Rh	[1,3–48,51,57–84,87–94,96,107,112–115,121,126,131,132]
Ni	[125]
Pd	[50,51,95,97–106,108–111]
Pt	[1,51–56]
Cu	[125]
Sn	[53–56,99]

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