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Application of transition metals in hydroformylation annual survey covering the year 2001

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Contents

Abstract

Hydroformylation in homogeneous and heterogeneous systems, and hydroformylation related reactions of carbon monoxide reported in 2001 are reviewed. © 2002 Elsevier Science B.V. All rights reserved.

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

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1. Hydroformylation

1.1. Homogeneous systems

1.1.1. Cobalt catalysts

The $CoBr_2$–Zn–CO–^tBuOH system was found to be useful as a catalyst precursor for the hydroformylation of olefins [1].

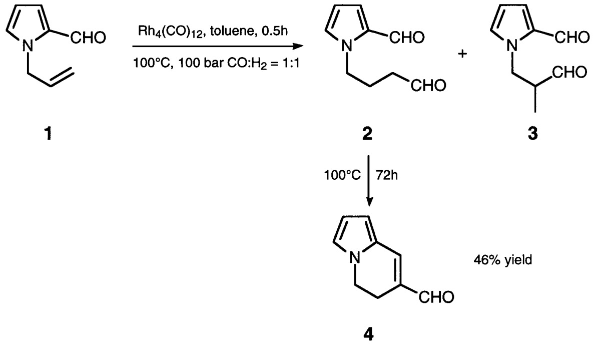
Cobalt carbonyls were prepared from an aqueous solution of cobalt(II) acetate in the presence of an organic solvent immiscible with water. The product in the organic phase was used as a hydroformylation catalyst [2].

The hydroformylation of cyclohexene catalyzed by $Co_2(CO)_6(PBu_3)_2$ was tested evaluating the conversion of the olefin in isochronous experiments carried out in the presence of an increasing pressure of an additional gas such as N_2, He, Ar, and Xe. Upon raising the partial pressure of the additional gas in the hydroformylation experiments, a significant drop of the product yields was observed in the case of N_2, Ar, and Xe. This has been regarded as a strong indication for an interaction of these gases with labile cobalt intermediates involved in the catalytic cycle [3]. A similar influence of additional gases on the rate of the ruthenium-catalyzed olefin isomerization has also been found [4].

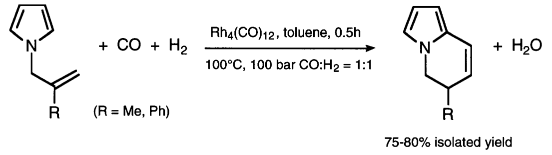
See also Ref. [68].

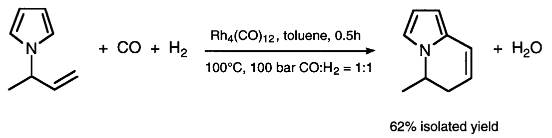
1.1.2. Rhodium catalysts

The kinetic control of the rhodium-catalyzed hydroformylation of **1** was found to give a 46:56 mixture of the corresponding aldehydes **2** and **3**. By heating the reaction mixture for longer times, even in the absence of CO and H_2, the linear aldehyde **2** disappears and 7-formyl-5,6-dihydro-indolizine (**4**) is obtained, whereas the branched aldehyde **3** remains unchanged [5].



5,6-Dihydroindolizines were selectively obtained in a one-pot hydroformylation/dehydration sequence in the presence of catalytic amounts of $Rh_4(CO)_{12}$ [6]. E.g.:





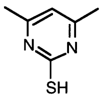
Rhodium-catalyzed hydroformylation of vinylfluoride followed by careful oxidation of the regiospecifically produced 2-fluoropropanal was found to afford 2-fluoropropanoic acid in about 70% yield [7].

The effect of *o*-alkyl-substituted triphenylphosphine ligands on the activity and regioselectivity in rhodium-catalyzed propene hydroformylation was studied. The effect of the process conditions on the activity and regioselectivity was investigated by varying the ligand-to-rhodium ratio (between 0 and 40), temperature (between 80 and 130 °C), and deactivation for some of the ligands. The results suggest that *o*-alkyl substituted triphenylphosphine ligands enhance the selectivity to isobutanal. However, the activity decreases at the same time. A correlation was found between the ^{31}P-NMR shifts of the ligands and the regioselectivity and -activity: as the shift decreases, the regioselectivity to isobutanal increases and the activity decreases [8]. The influence of the alkyl-substituted phosphines ((*o*-methyl-phenyl)diphenylphosphine, (*o*-ethylphenyl)diphenylphosphine, bis(*o*-methylphenyl)phenylphosphine, bis(*o*-ethylphenyl)phenylphosphine, and (2,4,5-trimethylphenyl)diphenylphosphine) was tested in rhodium-catalyzed 1-hexene hydroformylation. Compared with triphenylphosphine the alkyl-substituted phosphines were found to afford lower chemoselectivity towards aldehydes, but an increased normal to branched ratio [9].

A series of triphenylphosphine ligands modified with different heteroatom groups ($-SCH_3$, $-N(CH_3)_2$, $-OCH_3$, $-CF_3$) in the *ortho* or *para* position of the phenyl ring(s) were tested in the rhodium-catalyzed hydroformylation of 1-hexene and propene. The strong σ-donor ligands were found to yield higher hydroformylation activity than the less basic ligands [10].

The catalytic activity and selectivity of in situ prepared heterodonor phosphine rhodium catalyst were tested in the hydroformylation of ethyl acrylate, methyl methacrylate, styrene, 4-vinyl-1-cyclohexene, dicyclopentadiene and *cis*-1.2,3.6-tetrahydrophthalic anhydride. Systematic variation of the heterodonor atom in the *ortho* position of the ligand showed that the heterodonor atom has a significant influence on the activities and selectivities of the reaction. The activity seems to depend mainly on the modifying ligand, and the regioselectivity mainly on the structure and functionality of the alkene substrate. A clear regiocontrol was observed in the hydroformylation of α,β-unsaturated esters and styrene with an in situ formed *o*-(thiomethylphenyl)diphenylphosphine rhodium catalyst [11].

Carbonyl–triphenylphosphine–thiolate–rhodium complexes prepared from the corresponding thiols **5**, **6**, and **7** were found to be good catalysts in the hydroformylation of 1-heptene at 70 °C and 30 bar CO–$H_2 = 1{:}1$. The effects of the PPh_3–Rh ratio, the total reaction pressure, temperature and the solvent were studied. The donor capacity of mercaptopyrimidine ligands has been correlated with the activity of the catalysts. An increase in ligand basicity was found to give rise to a faster reaction [12].



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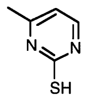

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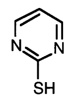
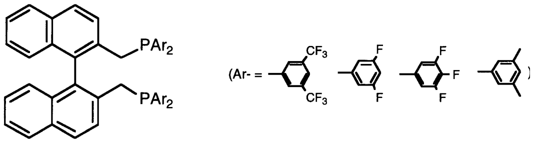


7

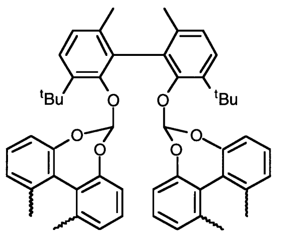
NAPHOS-type ligands **8** in combination with $Rh(CO)_2(acac)$ were found to induce excellent selectivities for the catalytic conversion of internal olefins (2-pentene, 2-octene) to linear aldehydes at 120 °C and 10 bar CO–$H_2 = 1{:}1$ [13].



8

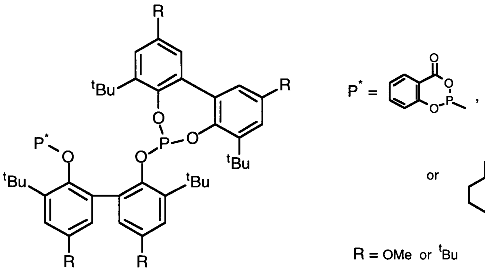
Linear long chain dialdehydes were prepared in 80–98% yields by hydroformylation of α,ω-diolefins and protected aldehydes having a terminal olefinic double bond using a $RhH(CO)PPh_3)_3$–XANTPHOS (1:3) catalyst system at 40–60 °C and 20 bar CO–$H_2 = 1{:}1$ [14]. The 9H-XANTHENE skeleton was used as a backbone for the construction of novel bulky diphosphite ligands with [1,1′-biphenyl]-2,2′-diyl linkers, which were found to form very selective and active rhodium catalysts for the hydroformylation of 1-octene, styrene, and (*E*)-2-octene [15].

The bisphosphite modified rhodium-catalyzed propene hydroformylation was investigated using (*RRR*)-**9** and (*SRS*)-**9** as the ligand in tetraglyme solution at 82 °C and 3 bar CO–$H_2 = 1{:}1$ pressure. Hydroformylation using (*SRS*)-**9** was found to result in a high regioselectivity (linear–branched ratio = 46) with an average rate of 513 turnovers h^{-1}. Under identical conditions, Rh-(*RRR*)-**9** gave a much lower rate (110 turnovers h^{-1} and regioselectivity (linear–branched ratio = 4) than the *SRS* diastereomer [16].



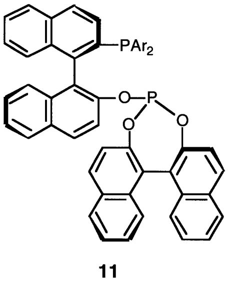
9

New phosphorus ligands, **10** have been synthesized and used for the rhodium-catalyzed hydroformylation of internal octenes at 130 °C and 20 bar CO–$H_2 = 1{:}1$, leading to > 93% aldehyde yield and 63.9–69.0% *n*-nonanal of the total aldehyde [17].



10

The effect of substituents in (*R*,*S*)-BINAPHOS derivatives (**11**) on the regio- and enantioselectivities in the rhodium-catalyzed asymmetric hydroformylation of styrene, 1-hexene, (*Z*)-2-butene and indene has been investigated. In comparison with (*R*,*S*)-BINAPHOS (Ar = Ph), the 3-methoxy-substituted ligand gave improved regio- and enantioselectivities at 60 °C for all olefins investigated. At 23 °C up to 95.0% *iso*-selectivity and up to 97.5% ee was achieved in the case of styrene hydroformylation [18].

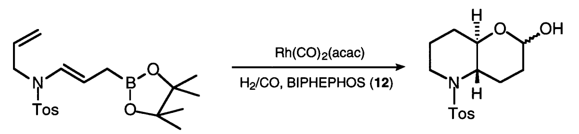


(Ar = Ph, 3-MeOC_6H_4, $3\text{-}^i\text{PrO-C}_6H_4$, $3\text{-C}_6F_{13}CH_2CH_2C_6H_4$, $3,5\text{-(MeO)}_2C_6H_3$, 4-MeO-C_6H_4, 3-Me-C_6H_4)

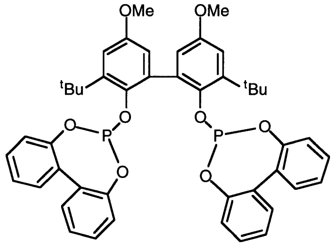
11

Density-functional theory calculations were used to study the rhodium-complex intermediates in the asymmetric hydroformylation of styrene with the Et–DuPHOS analog model phosphine. The energies of the two-enantiomer models were found to differ by 11.3 kcal mol^{-1} [19].

N-Allyl-(*E*)-γ-aminoallyl boronates in the presence of an in situ prepared rhodium–BIPHEPHOS (**12**) catalyst under hydroformylation conditions (60 °C, 5 bar CO–$H_2 = 1{:}1$) were found to enter into a domino hydroformylation–allylboronation–hydroformylation reaction cascade to generate bicyclic *N*,*O*-heterocycles [20]. E.g.:

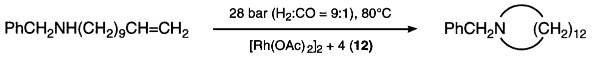


80% isolated yield

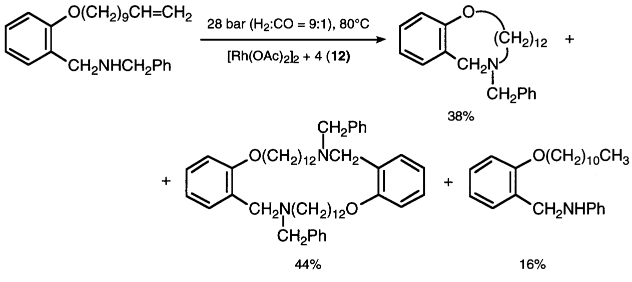


12

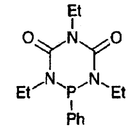
The synthesis of medium and large cyclic amines in rhodium-catalyzed reactions of aminoalkenes with H_2/CO has been described [21]. E.g.:



85% isolated yield



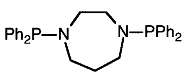
The mechanism of the rhodium-catalyzed hydroformylation reaction using a monodentate phosphorus diamide ligand **13** was investigated by kinetic and spectroscopic techniques. The kinetic study revealed that the rate-determining step of the hydroformylation reaction is strongly dependent on the reaction conditions used. The results of in situ high pressure IR and NMR studies have shown that the rhodium hydride complex $HRhL_2(CO)_2$ and several rhodium–acyl complexes are present in solution during the hydroformylation reaction. The major rhodium–acyl complex formed, $RC(O)RhL_2(CO)_2$, has a trigonal–bipyramidal structure with the two phosphorus ligands coordinated in the equatorial plane. From the results of deuterioformylation experiments it was concluded that the regioselectivity of the reaction is determined in the hydride migration step [22].



13

The intramolecular hydroformylation of allyldiphenylphosphine using the monodentate phosphorus diamide (**13**) based rhodium catalyst was studied. Coupling of the ligand and substrate functions stabilized the intermediates of the hydroformylation reaction and enabled the characterization of the complexes using NMR spectroscopy [23].

The highly electron rich bidentate phosphine ligands **14**, **15** and **16** were tested in the rhodium-catalyzed hydroformylation of 1-hexene at 100 °C and 20 bar $CO-H_2 = 1:1$. Ligand **16** was found to give the most active catalyst leading to 98.9% conversion of 1-hexene with a 95.5% aldehyde selectivity. The linear–branched aldehyde ratio is 1.2 [24,25].



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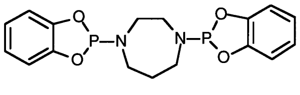

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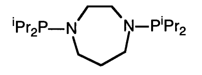
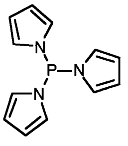


16

Hydroformylation of 1-undecene in the presence of a triazenidorhodium complex $Rh(Ph_2N_3)(CO)(PPh_3)_2$ as the catalyst precursor was studied in several solvents at 1 bar $CO-H_2 = 1:1$. In the temperature range from 30 to 60 °C the maximum yield of aldehydes were obtained at 50 °C [26].

Various pyrrolyl-, indolyl-, and carbazolylphophines were tested as ligands in the rhodium-catalyzed hydroformylation of 2-pentene. The best normal (*n*)–*iso* (*i*) ratios of about 60:40 were found at low synthesis gas pressure (10 bar) in the presence of ligand **17** [27].

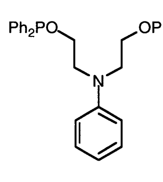


17

A rhodium–pyridylphosphine catalyst encapsulated with zinc(II) porphyrin was found to be an order of magnitude more active in 1-octene hydroformylation at 25 °C than the same catalyst but without the porphyrin complex. With the encapsulated catalyst the branched aldehyde product is preferentially formed (linear–branched = 0.6 at 25 °C and 20 bar $CO-H_2 = 1:1$) [28].

New cationic rhodium(I) complexes with hemilabile nitrogen-containing bis(phosphinite) or bis(phosphine) ligand **18** or **19**, respectively, were used for the hydroformylation of styrene. Chemoselectivities for aldehydes up to 99.7% and regioselectivities towards the branched aldehyde up to 96.1% were observed [29].

A cationic rhodium(I) complex with hemilabile *N*,*P*,*N*-ligand **20**, possessing four methoxy groups has been tested as a catalyst in hydroformylation of styrene. Turnover numbers up to 1407 mol aldehyde/mol rhodium, and a high chemoselectivity for aldehydes (> 97%) with a very good branched–linear ratio (up to 95.2%) were observed [30].



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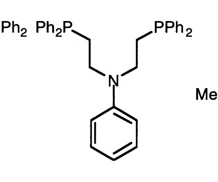

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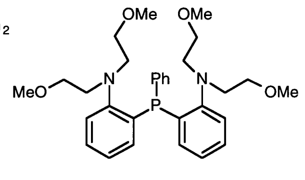
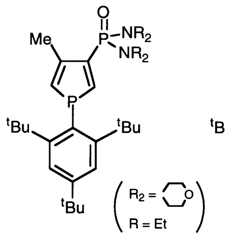


20

The phosphorylated phospholes **21**, **22**, **23** were tested as ligands in rhodium-catalyzed styrene hydroformylation at 100 °C and 80 bar CO–H_2 = 1:1. The aldehyde selectivity was found to be higher than 99% in all cases with a branched aldehyde selectivity of up to 80% [31].



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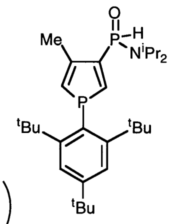

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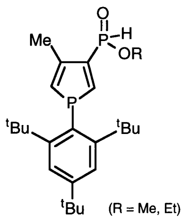
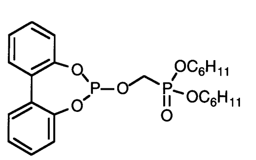


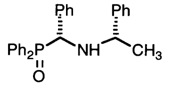
23

High activity and a high *i–n* aldehyde ratio (97:3) was observed in the rhodium-catalyzed hydroformylation of styrene at 25 °C and 40 bar CO–H_2 = 1:1 if the catalyst was modified with the phosphite–phosphonate ligand **24** [32].



24

Enantiomerically pure single *N*,*P*(*O*) diastereomer (**25**) and a 1:1 mixture of two *N*,*P*(*S*) diastereomers (**26**) have been tested in the rhodium-catalyzed hydroformylation of styrene. Using **25** high activities and regioselectivities but no enantioselectivity were observed at 55 °C and 27–34 bar CO–H_2 = 1:1 [33].



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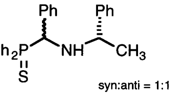
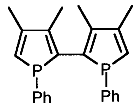


26

Hydroformylation of a mixture of isomeric octenes to C_9-aldehydes catalyzed by the rhodium–triphenylphosphine oxide system was studied. The yield of C_9-aldehydes was found to increase with the increase of the P–Rh ratio when the ratio of P–Rh was below 20. About 90% yields of C_9-aldehydes were obtained at 140 °C and 105 bar syngas pressure using $Rh(OAc)_2$ and $Ph_3P=O$ as the precatalyst [34]. The effects of ammonium salts as additives in the $Rh(OAc)_2$–$Ph_3P=O$ catalytic system on the hydroformylation of mixed octenes were studied. Ammonium salts such as $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)_2CrO_4$, $(NH_4)_2Cr_2O_7$, and $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ were found to increase the yield of isononyl aldehydes and decrease the loss of rhodium in the distillation process of the products [35].

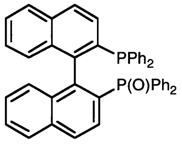
Excellent regioselectivities in branched aldehyde (98%) have been observed in hydroformylation of styrene at 25 °C and 150 bar CO–H_2 = 1:1 using a racemic mixture of the rhodium complexes [Rh(**27**)(COD)]BF_4 as the catalyst precursor [36].



27

The olefin insertion into the rhodium–hydrogen bond as the step determining the regioselectivity of rhodium-catalyzed hydroformylation of propene, 2-methylpropene, 1-hexene, 3,3-dimethylbutene, fluoroethene, 3,3,3-trifluoropropene, vinylmethylether, allylmethylether and styrene has been investigated by comparison of theoretical and experimental results. The various $HRh(CO)_3$(olefin) complexes were examined at the B3P86/3-21G or /6-31G* level (LANL2DZ for rhodium). The activation energies for the alkyl rhodium intermediate formation, computed at either level, along the pathways to branched or linear aldehydes allow the prediction of the regioselectivity ratios, which are in good agreement with the experimental values evaluated for the isomeric aldehydes [37]. The origin of regioselectivity in rhodium diphosphine catalyzed hydroformylation was investigated by means of hybrid QM/MM calculations using the IMOMM method. The roles of the diphosphine bite angle and the nonbonding interactions were analyzed in detail by considering rhodium systems containing XANTPHOS-type ligands. Calculations have revealed that regioselectivity is governed by the nonbonding interactions between the diphenylphosphino substituents and the substrate. Effects directly associated to the bite angle have a smaller influence [38].

Rhodium complexes with the axially chiral phosphinyl phosphine (*S*)-**28** were found to be active but poorly stereoselective catalysts among others in hydroformylation of alkenes [39].



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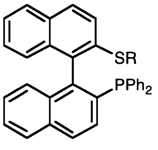
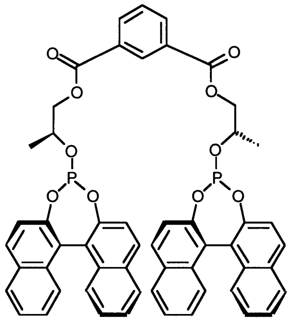


29

The *S*-methyl or the *S*-isopropyl derivatives **29** have been used as chiral ligands in the rhodium(I)-catalyzed asymmetric hydroformylation of styrene. Using the (*R*)-isopropyl sulfide at 40 °C and 60–120 bar $CO-H_2 = 1:1$ pressure resulted in up to 96% branched selectivity at 100% conversion, but in low stereoselectivity of (*S*)-2-phenyl-propionaldehyde (14% ee). Using the (*R*)-methyl sulfide under the same conditions gave only 90% branched aldehyde which was practically racemic (2% ee) [40].

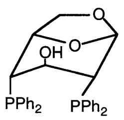
In situ high pressure spectroscopic techniques were used to study the species present in the hydroformylation of styrene by rhodium diphosphine (BDPP and CHIRAPHOS) system. It was found that the $[RhH(CO)_2(P-P)]$ species are the resting state observed in the case of BDPP and CHIRAPHOS under hydroformylation conditions and the presence of a monophosphine or an excess of diphosphine does not result in formation of other species [41].

The rhodium-catalyzed asymmetric hydroformylation of vinylarenes using the chiral diphosphite ligand **30** was found to produce up to 81% regioselectivity in the branched aldehyde and up to 76% ee of the *R*-isomer at 40 °C and 15 bar $CO-H_2 = 1:1$ [42].



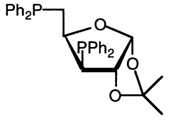
30

A new chiral ligand **31** prepared from D-glucose was used as the ligand in rhodium-catalyzed asymmetric hydroformylation of vinylacetate, styrene and norbornene at 60–80 °C and 60 bar $CO-H_2 = 1:1$. The best results, up to 96% yield of aldehydes (branched–normal up to 96:4) and 92–93% ee, were obtained with vinylacetate as the olefin substrate. The results for styrene and norbornene were found to be much less satisfactory, 63–68 and 22–25% ee, respectively. The high enantio- and regioselectivity in the hydroformylation of vinylacetate is explained in terms of the hydrogen bonding between the OH group in the ligand molecule and the carbonyl group in the vinylacetate [43].



31

Furanoside diphosphines **32**–**34** derived from D-(+)-xylose and D-(+)-glucose were tested as ligands in rhodium-catalyzed asymmetric hydroformylation of vinylarenes. High regioselectivities up to 97% for the branched aldehydes and enantioselectivities of up to 58% ee were observed [44].



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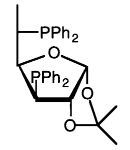

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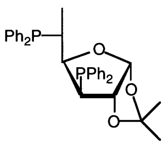


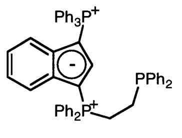
34

A series of novel diphosphite ligands derived from D-(+)-glucose have been used for the rhodium-catalyzed hydroformylation of vinylarenes. Both excellent regioselectivities (up to 98.8%) and enantioselectivities (up to 91%) were achieved under mild conditions. Results of systematic variation in the configuration of the ligand show that the absolute configuration of the product is governed by the configuration at the sterogenic center C(3), while the level of the enantioselectivity is influenced by a cooperative effect between stereocenters C(3) and C(5). Based on in situ NMR and IR investigations a correlation between the structure of the $[HRh(CO)_2(PP\text{-}ligand)]$ species and their enantiodiscriminating performance in hydroformylation was found. Enantioselectivities are highest with ligands with a strong bis-equatorial coordination preference [45].

Rhodium diphosphine systems using the diphosphines CHIRAPHOS, BDPP, DIOP, BINAP, and BPPFA were used as catalyst precursors for the hydroformylation of 2,5-dihydrofuran. The high regioselectivity observed in the tetrahydrofuran-3-carbaldehyde (up to 100%) was found to decrease by increasing the temperature or by using lower pressure of CO/H_2 and lower diphosphine–[Rh] molar ratio. The effect of pressure and temperature was explained in terms of an isomerization process via β-elimination during the hydroformylation of 2,5-dihydrofuran [46].

Phosphabenzenes as monodentate π-acceptor ligands have been tested in rhodium-catalyzed hydroformylation of 1-octene and internal alkenes. The catalytic performance was found to be determined by steric influences. Turnover frequencies of up to 45 370 h^{-1} for the hydroformylation of 1-octene were measured. The reactivity differences between the phosphabenzene and the triphenylphosphine catalyst was found to increase on going to the more highly substituted alkenes. Thus, tetra-substituted alkenes can be hydroformylated in the presence of the phosphabenzene catalyst, whereas the triphenylphosphine system fails to give any product [47].

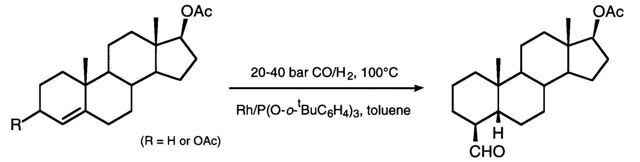
Rhodium complexes of a chelating bisphosphoniobenzophospholide cation **35** were found to be active catalysts of 1-hexene hydroformylation at 20 °C and 40 bar $CO–H_2 = 1:1$, with high chemoselectivity to aldehydes but poor linear–branched regioselectivity [48].



35

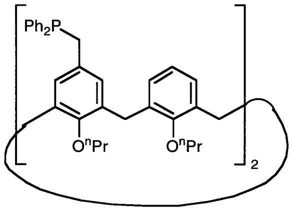
Immobilization of a catalytically active rhodium complex by electrostatic interactions of tris(sodium-*m*-sulfonatophenyl)phosphine ligands with a soluble polyelectrolyte has been achieved by using poly(diallyldimethyl ammonium tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate as the polyelectrolyte. The polyelectrolyte-bound catalyst was found to be active for hexene hydroformylation and can be recovered and recycled by ultrafiltration [49].

Hydroformylation of **36** (R = H or OAc) using a rhodium tris(*O*-*tert*-butylphenyl)phosphite catalyst was found to give in both cases **37** as the major reaction product. This reaction was claimed to be the first example of a catalytic carbonylation to the β-face of a steroid backbone [50].



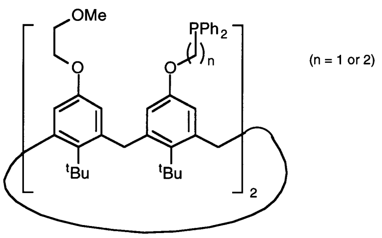
36 **37**

A di-rhodium complex obtained by combining $[Rh(COD)Cl]_2$ with a new upper-rim phosphacalix[4]arene (**38**) has been found to be an active catalyst for the hydroformylation of 1-octene and styrene at 70 °C and 55 bar $CO–H_2 = 1:1$. For 1-octene a linear–branched aldehyde ratio of 2.21–2.48, and that for styrene 0.16 was obtained [51].



38

Rhodium complexes with calix[4]arene-derived diphosphinites **39** were found to catalyze the hydroformylation of styrene at 40 °C and 40 bar $CO–H_2 = 1:1$ leading to a 95:5 ratio of the 2- and 3-phenylpropanal products [52].

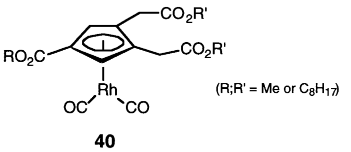


39

The synthesis of electron poor calix[4]arene based phosphorus diamides and phosphites and their application in the hydroformylation of 1-octene was described. Depending on the reaction conditions yields up to 99% and *n*–*iso*-selectivities between 0.7 and 2.6 were observed [53].

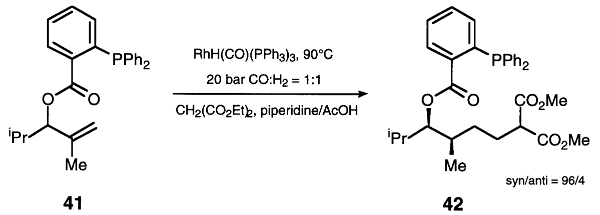
Dendrimers based on polyhedral oligomeric silsesquioxane cores with 16 PPh_2 groups on the periphery were found to give much higher linear selectivities (up to 14:1) than their small molecule analogues (3–4:1) as ligands in the rhodium-catalyzed hydroformylation of 1-octene at 120 °C and 10 bar $CO–H_2 = 1:1$ [54].

Half-sandwich rhodiumdicarbonyl complexes containing trisubstituted cyclopentadienyl ligands (**40**) have been used as catalysts for the hydroformylation of styrene. At 100 °C and 70 bar $CO–H_2 = 1:1$ the corresponding linear and branched aldehydes (58:42 ratio if R = R′ = Me) were obtained in up to 99% yield [55].



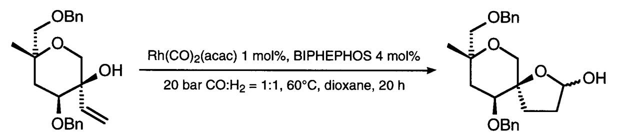
40

A rhodium–phosphine-catalyzed domino hydroformylation–Knoevenagel reaction–hydrogenation process was found to convert the methallyl *ortho*-diphenylphosphonylbenzoate (±)-**41** in the presence of diethylmalonate and piperidinium acetate into the substituted malonate (±)-**42** in satisfactory yield (51%) and with good diastereoselectivity [56].

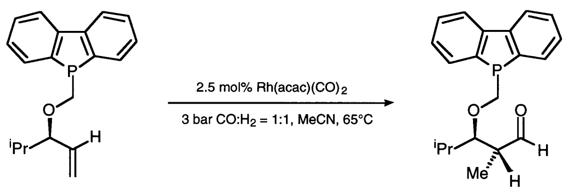


41 **42**

Spirocyclic hemiacetals were prepared from the corresponding allylic alcohol precursors by rhodium-catalyzed hydroformylation [57]. E.g.:

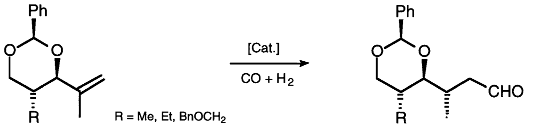


An effective directing group strategy for the branched-selective rhodium-catalyzed hydroformylation of allylic ethers has been developed by using the dibenzophosphole group [58]. E.g.:



94% isolated yield of aldehydes
98:2 = branched:linear
94:6 = anti:syn

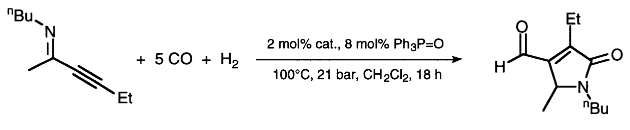
An anti-selective hydroformylation of 2-propylidene-substituted 1,3-dioxanes (**43**) with excellent levels of acyclic stereocontrol has been obtained by using 0.7 mol% [$Rh(CO)_2(acac)/4P(OPh)_3$] as the catalyst precursor in toluene solution at 70 °C and 20 bar $CO-H_2 = 1:1$ [59].



43

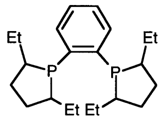
dr ≥ 99:1 R = Me, Et
dr = 95:5 R = BnOCH$_2$

The tandem cyclohydrocarbonylative/CO insertion of α-imino alkynes in the presence of catalytic amounts of the zwitterionic rhodium complex (η^6-$C_6H_5BPh_3)^-Rh^+(COD)$ and $Ph_3P{=}O$ was found to afford aldehyde substituted pyrrolinones in 67–82% yields [60]. E.g.:



82% isolated yield

The rhodium-catalyzed styrene hydroformylation in supercritical carbon dioxide was studied using $[(COD)Rh(\mathbf{44})]^+[\mathbf{45}]^-$ as the catalyst precursor. No enantioselectivity but a change of the reaction rate and the selectivity was observed by changes in pressure at constant temperature. Estimated partial molar volumes were used to predict the experimentally observed selectivity behavior [61].



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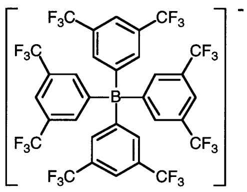
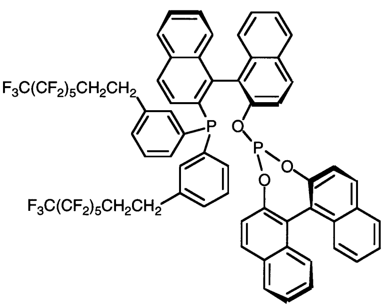


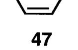
45

Novel fluorous $[R_f(CH)_2]_2$–BINAPHOS ligands ($R_f = n$-C_4F_9 and n-C_6F_{13}) were prepared and tested as ligands in the rhodium-catalyzed asymmetric hydroformylation of styrene. These new fluorous chiral ligands when used with a rhodium catalyst were found to achieve comparable or even higher regio- and enantioselectivity in the asymmetric hydroformylation of styrene in benzene or perfluorotoluene at 60 °C and 40 bar $CO-H_2 = 1:1$, as compared to those by the Rh–BINAPHOS system. Using supercritical CO_2 as the solvent with the new ligands at 60 °C and 100 bar total pressure ($CO-H_2 = 1:1$, 20 bar) the rhodium-catalyzed hydroformylation of styrene gave 89:11–90:10 regioselectivity and 70–74% ee [62]. The ligand (*R*,*S*)-**46** was found to form a highly efficient enantioselective rhodium catalyst for hydroformylation of vinylarenes, norbornadiene, indene, vinylacetate, and allylacetate in supercritical carbon dioxide. The best results for styrene and vinylacetate are 93.6 and 95.4% ee, respectively [63].

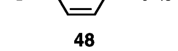


46

A series of inexpensive alkoxycarbonylated arylphosphines, such as **47**, were examined in the rhodium-catalyzed hydroformylation of 1-decene, styrene, and methyl acrylate in supercritical carbon dioxide, in an attempt to replace the expensive fluoroalkylated phosphines. Results obtained at 80 °C, 20 bar $CO-H_2 = 1:1$ and 180 bar CO_2 using the combination of $Rh(CO)_2$(acac) and 10 equiv. of ligand **47** was found to be comparable with that obtained with ligand **48** [64].



47



48

Dramatic 10–20-fold rate enhancements were observed by changing the reaction medium from toluene to supercritical carbon dioxide in the hydroformylation of alkyl acrylates catalyzed by rhodium–P(4-$C_6H_4C_6F_{13})_3$ complexes [65].

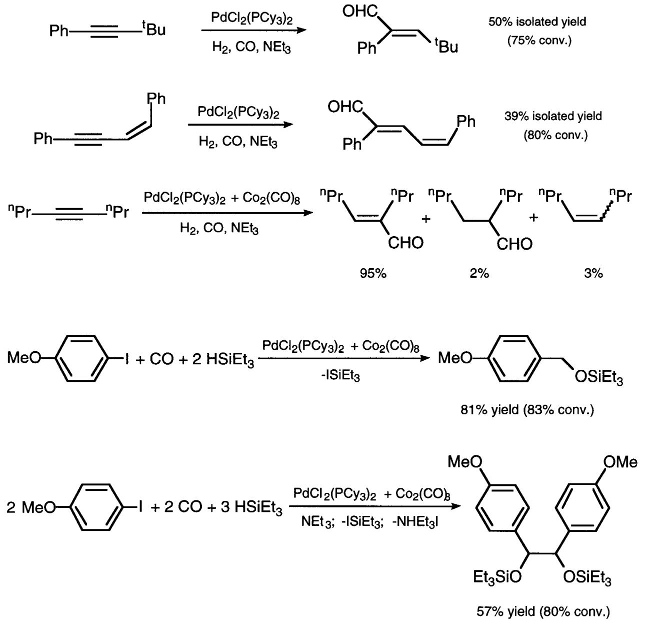
See also Refs. [71,73,77,79,80,87–89,92,94,95,127].

1.1.3. Other metals as catalysts and bimetallic catalysts

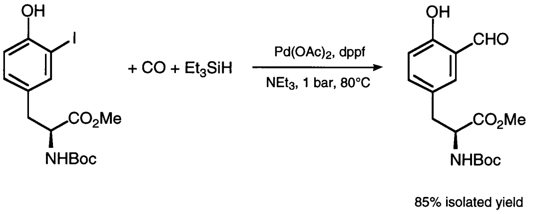
The cluster complex $[Re_2Rh(\mu\text{-}PCy_2)(\mu\text{-}CO)_2(CO)_8]$ was found to be an active catalyst in hydroformylation of 1-hexene at 30 °C and 4 bar $CO–H_2 = 1:1$ leading to the *n*- and *iso*-aldehyde product with 58 and 26 h^{-1} turnover frequency, respectively. The analogous dimanganese–rhodium complex $[Mn_2Rh(\mu\text{-}PCy_2)(\mu\text{-}CO)_2(CO)_8]$ was found to be much less active in hydroformylation under the same conditions [66].

Ruthenium carbonyl derivatives with the bulky diphosphine ligands 1,2-bis[bis(pentafluorophenyl)phosphino]ethane and bis(dicyclohexylphosphino)methane were found to show higher activities in hydroformylation of ethylene and propylene at 80 °C and 20 bar $CO–H_2 = 1:1$ than those observed for $Ru_3(CO)_{12}$ and $Ru_3(CO)_{10}(dppe)$ [67].

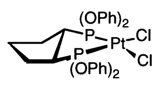
The palladium complex $PdCl_2(PCy_3)_2$ was found to work as a regio- and chemoselective catalyst for the hydroformylation of internal alkynes at 150 °C and 70 bar $CO–H_2 = 1:1$ to give the corresponding α,β-unsaturated aldehydes. The combined use of $PdCl_2(PCy_3)_2$ and $Co_2(CO)_8$ improves the catalytic activity with little change of selectivity. The bimetallic catalyst $PdCl_2(PPh_3)_2–Co_2(CO)_8$ was found to be effective for the carbonylation of aryl iodides with CO/HSiEt$_3$ at 80 °C and 50 bar CO. The addition of NEt$_3$ to the reaction system results in the formation of 1,2-diaryl-1,2-disiloxyethanes [68]. E.g.:



Palladium-catalyzed hydroformylation of 3-iodo-L-tyrosine derivatives at 80 °C and 1 bar CO in the presence of Et$_3$SiH and NEt$_3$ was found to give the corresponding aldehyde quantitatively [69]. E.g.:



Platinum complexes of cyclopentane-based C_2 chiral bis(phosphonite) (**49**) and bis(phosphine) (**50**, **51**) were found to be catalysts for the hydroformylation of styrene, if activated by SnCl$_2$. The chemoselectivity in the formation of aldehydes at 100% conversion is relatively low (34–49%) because hydroformylation is always followed by hydrogenation of the initially produced aldehydes to the corresponding alcohols. With ligand **49** and **50** in the catalytic systems, the unbranched aldehyde undergoes consecutive reduction faster than the branched product, which accounts for the high regioselectivity towards the branched aldehyde (branched–normal ratios ≥91:9). Tin-modified platinum complexes with (*R*,*R*)-**49**, (*S*,*S*)-**49**, and (*S*,*S*)-**50** ligands give only low (ee <18%) stereoselectivity for asymmetric hydroformylation [70].



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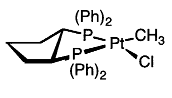

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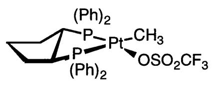
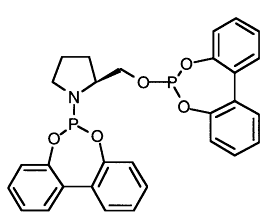


51

The chiral aminophosphonite–phosphite ligands **52** and **53** were evaluated in the platinum/SnCl$_2$- and rhodium-based hydroformylations of styrene. Generally, only modest enantioselectivities were obtained and for the platinum-based reactions, the highest asymmetric induction (44% ee, branched–normal = 53:47) was found when the temperature was lowered to 20 °C, but even in this case the hydrogenation side-reaction was up to 34% [71].



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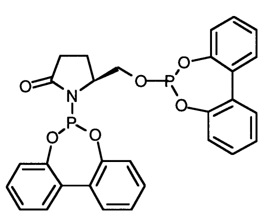
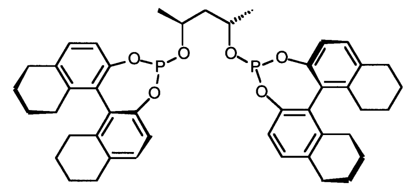


53

High enantioselectivities (86–91% ee) were obtained in the asymmetric hydroformylation of styrene using a platinum(II)–SnCl$_2$ catalytic system containing the ligands **54** and **55** [72].



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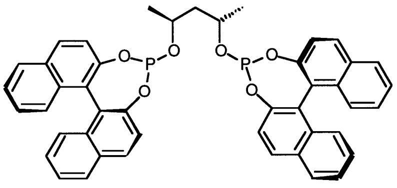
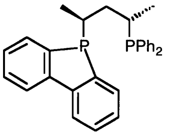


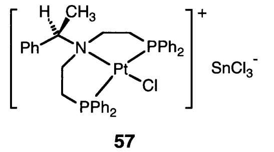
55

The novel chiral phosphine–phosphole **56** has been used as a ligand in the platinum/tin-catalyzed asymmetric hydroformylation of styrene. High regioselectivity (89:11 *i*–*n* aldehyde ratio) and high enantioselectivity (88% ee) of the branched aldehyde was observed at 24 °C and 155 bar pressure ($CO-H_2 =$ 9:1). The in situ prepared catalyst from $Rh(CO)_2(acac)$ and **56** led to a 92:8 *i*–*n* aldehyde ratio and 47% ee in styrene hydroformylation at 40 °C and 30 bar $CO-H_2 = 1:1$ pressure [73].



56

The catalytic activity of a cationic platinum complex **57** with enantiopure (*R*)-*N*,*N*-bis-(2-diphenylphosphinoethyl)-1-phenyl-ethyl amine ligand in the hydroformylation of styrene was found to be low at 100 °C and 70 bar $CO-H_2 = 1:1$ leading to an optical induction of 20–24% [74].



57

See also Refs. [14,75].

1.2. Heterogeneous systems

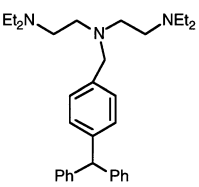
1.2.1. Supported complexes

A bimetallic catalyst derived from $Ru_3(CO)_{12}$ and $Co_2(CO)_8$ with a 3:1 Co–Ru atomic ratio on silica support was found to show significant improvement of hydroformylation activity with respect to monometallic catalysts [75].

Heterogenized rhodium catalysts based on resin-bound dendritic arms having differently exposed surroundings around the phosphine ligands have been compared as catalysts in hydroformylation of styrene, *p*-methoxystyrene, and vinylacetate or vinylbenzoate at 45 °C and 70 bar $CO-H_2 = 1:1$ in several repeated cycles. High reactivity was found. The catalyst exhibits > 99% conversion to the product aldehydes (branched–linear = 14:1–19:1) even up to the sixth cycle in the case of styrene hydroformylation. The catalyst that bears the phosphine ligands on arms exhibits an enhanced recycling potential when compared to a similar catalyst that bear the phosphine ligands on the ends of the arms [76].

Rhodium thiolate complexes tethered to delamellated γ-zirconium phosphate were used as catalyst in 1-heptene hydroformylation. The heterogeneous hydroformylation with the rhodium thiolate supported catalyst at 70 °C and 8 bar $CO-H_2 = 1:1$ was found to be faster and more selective towards the linear aldehyde product than the process performed with the rhodium complex in homogeneous media [77]. An α-zirconium phosphate supported phosphine (**58**) rhodium complex was tested as a catalyst in continuous gas-phase hydroformylation of propene and in liquid phase hydroformylation of 1-hexene. The catalyst was found to be efficient in the gas-phase hydroformylation of propene but with a rather low regioselectivity (*n*–*i* = 1.7:2.4). The catalyst performance with respect to liquid phase hydroformylation of 1-hexene is poor [78].

Hydroformylation of 1-heptene in toluene was studied using the rhodium(I) pentafluorophenylthiolate complex $[Rh(\mu\text{-}SC_6F_5)(COD)]_2$ and $[Rh(\mu\text{-}SC_6F_5)(CO)_2]_2$ anchored on phosphinated silica as the immobilized catalysts. The reaction rate with the immobilized catalysts was lower than that observed for the homogeneous counterparts. However, activity is maintained for several cycles [79].



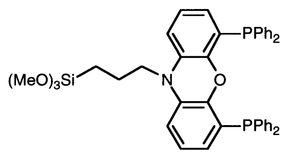
58

The rhodium complex $[Rh(COD)Cl]_2$ supported on activated carbons was used as a catalyst for the hydroformylation of 1-octene. The effects of support surface chemistry and the solvent used as reaction media (hexane, acetone or methanol) on the activity and selectivity to linear products were investigated. The highest stability of the catalyst was found in hexane. The heterogenized complex shows a conversion level higher or similar to that of the homogeneous complex and with a higher selectivity to the linear products [80].

The influence of the hydration and the surface characteristics of five different supports in the hydroformylation of 1-octene by supported aqueous phase catalysis using $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ as the catalyst was studied. The size of the pores and the amounts of water were found to be the determining factors [81].

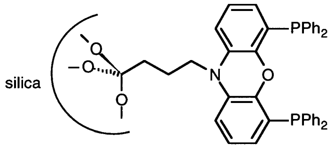
Immobilization of a dinuclear rhodium(II) acetato complex with bridging *ortho*-metalated phosphine ligands on amorphous silica supports as well as a mesoporous MCM-41 support resulted in useful catalysts for hydroformylation of styrene and 1-decene. The effect of recycling on the conversion of the olefins and on the branched–normal selectivity of the hydroformylation products was studied [82].

A polysilicate immobilized rhodium complex with ligand **59** was found to perform as a selective hydroformylation catalyst showing an overall selectivity for the linear aldehyde of 94.6% in the case of 1-octene hydroformylation at 80 °C and 50 bar $CO–H_2 = 1:1$. In addition the formation of 1-nonanol (3.6% at 20% conversion) was observed via the hydrogenation of the corresponding aldehyde. The addition of 1-propanol completely suppresses the reduction reaction. The reduction reaction becomes prevalent if the atmosphere is changed from CO/H_2 to H_2. Thus, by simple changes in the reaction conditions, a reversible switching of the catalyst mode between a hydroformylation, a hydrogenation and a hydroformylation/hydrogenation cascade catalyst was demonstrated [83].



59

The immobilization of a homogeneous hydroformylation catalyst on silicon or silicon carbide monoliths, constructed as the blades of a mechanical stirrer, has been reported as a novel concept towards sustainable catalyst systems. A rhodium complex containing a XANTHENE-based diphosphine ligand **60** was covalently anchored directly to the silicon-monoliths or via silica coating to silicon carbide monoliths. In the hydroformylation of 1-octene an overall selectivity of 89±3% for the linear aldehyde was observed. The extremely stable catalyst shows no deterioration within 6 months and can be applied for a whole range of substrates as well as in liquid organic, liquid aqueous, and gas phase reactions within one reactor and with the same batch of catalyst [84].



60

Hydroformylation of 1-hexene in the presence of a $[Rh(COD)(2\text{-}picoline)_2]PF_6$ catalyst immobilized on poly(4-vinylpyridine) was studied in 80% aqueous 2-ethoxyethanol under water–gas shift reaction conditions. The effect of the 1-hexene–catalyst ratio (16:105), carbon monoxide partial pressure (0.6–1.8) and temperature (70–110 °C) on the turnover frequency of CO_2, isomeric hexenes and aldehydes was investigated [85].

1.2.2. Biphasic systems

Rhodium complexes with modified polyether ligands were found to show high catalytic activity in aqueous hydroformylation of 1-dodecene at 50 °C and 15 bar $CO–H_2 = 1:1$ [86].

Rhodium-catalyzed hydroformylation in toluene or in the biphasic system toluene–water or cyclohexane–water of 1,1-bis(*p*-fluorophenyl)-2-propenol and of 1,1-bis(*p*-fluorophenyl)-2-propynol was used in a key step in the synthesis of two neuroleptic agents, Fluspirilen and Penfluridol [87].

The rhodium complex $[Rh(\mu\text{-}SCH_2)_{10}CO_2Na)(COD)]_2$ and $[Rh(\mu\text{-}S(CH_2)_{17}COOH)(COD)]_2$ were found to be highly efficient catalysts for olefin hydroformylation in a biphasic system (water–organic bilayer) and in a homogeneous system (THF), respectively. The pH-dependent solubility of the complexes allows a simple recovery process for their recycling [88].

The Rh/TPPTS-catalyzed hydroformylation of *N*-allylacetamide in water was found to proceed at a much faster rate and in a much higher selectivity (>99%) towards the aldehydes, 4-acetamidobutanal and (*Z*)-methyl-3-acetamidopropanal, than the Rh/PPh_3-catalyzed reaction in organic solvents, such as THF, toluene and methanol. In water at 90 °C and 50 bar H_2/CO, turnover frequencies $>10\,700\ h^{-1}$ are observed at the optimum pH of 7.0. At pH 11.0 the linear–branched ratio increases to 6.5, while the overall selectivity towards the aldehydes decreases to 41%. In a toluene–water biphasic system, owing to the presence of water, the selectivity towards the aldehydes remains >99% [89].

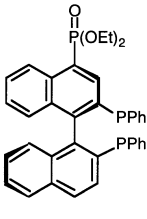
Rhodium-catalyzed hydroformylation of hexene in an optimized microemulsion containing sodium dodecylsulfate as a detergent was studied. High conversions (about 97%) and high yields of aldehydes (>94%) with a *n*–*i* ratio of 2.2:2.5 were obtained [90].

The hydroformylation of 1-dodecene was studied using the water-soluble rhodium complex [RhCl(CO)(TPPTS)$_2$] as the catalyst precursor in the presence of TPPTS, TPPDS and cetyltrimethylammonium bromide. A synergistic effect between TPPTS and TPPDS on the regioselectivity of 1-dodecene hydroformylation was observed. The selectivity for the linear aldehyde in the product was found to be 95.7% at the molar ratio of [TPPTS]–[TPPDS] = 0.5 [91].

Rh(CO)$_2$(acac)/sulfonated-XANTPHOS dissolved in a 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid was found to catalyze the hydroformylation of C_8–C_{12} olefins with up to 99% selectivities in aldehydes [92].

The effect of pH on the reactions of [RhCl(TPPMS)$_3$] and *trans*-[RhCl(CO)(TPPMS)$_2$] with dihydrogen in the presence of free TPPMS was investigated. The formation of Rh(CO)H(TPPMS)$_3$ was found to be strongly pH dependent in the pH 5–9 range. This provides an explanation for the observed but previously unexplained pH dependence of several aqueous phase hydroformylation reactions [93].

Mono- and bisphosphorylated BINAP derivatives (**61**–**66**) were tested as ligands in both homogeneous and aqueous biphasic rhodium-catalyzed hydroformylation of styrene and vinylacetate. High chemo- and regioselectivities were observed. Compared with catalysts prepared by the parent BINAP ligand the enantioselectivity in the hydroformylation of vinylacetate was found to be slightly increased using the phosphorylated ligands **61** and **62**. The enantiomeric excess obtained with the catalyst made of **65** and Rh(CO)$_2$(acac) is the highest one (27% ee) obtained so far in the aqueous biphasic hydroformylation of styrene [94].



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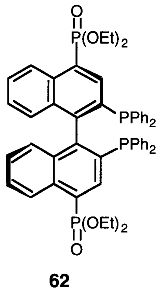

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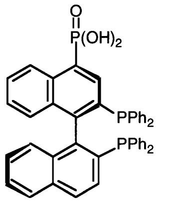

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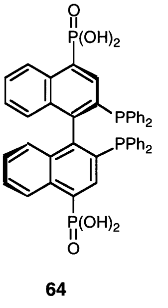

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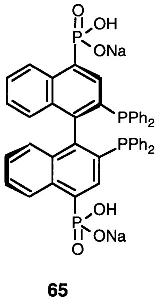

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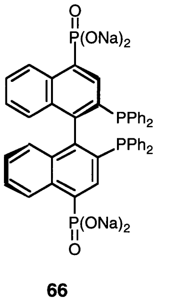
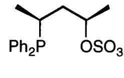


66

Water-soluble rhodium/phosphonate–phosphine catalysts were found to be highly active and selective for the biphasic hydroformylation of 1-octene at 100 °C and 30 bar CO–H_2 = 1:1. In the case of ligand $Ph_2P(CH_2)_{10}PO_3Na_2$ with EtOH as co-solvent 1050 h^{-1} turnover number and 97% aldehyde selectivity (n–i aldehyde ratio = 2.6) is achieved [95].

Rhodium complexes of a new type of water-soluble mono- and ditertiary phosphines (**67** and **68**) bearing-SO_3Li groups were used for liquid biphasic hydroformylation of styrene and 1-octene. The use of **67** in the hydroformylation of styrene at 60 °C resulted in high regioselectivity toward the branched aldehyde (90%). However, no optical induction was observed [96].



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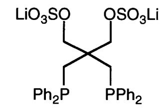
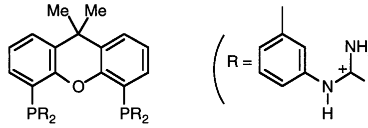


68

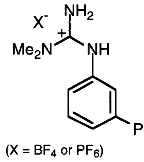
The rhodium-catalyzed hydroformylation of 1-octene in a 1-butyl-3-methyl-imidazolium hexafluorophosphate solvent was investigated. The new guanidinium-modified diphosphine ligand with a XANTHENE backbone (**69**) in combination with Rh(CO)$_2$(acac) was found to show high regioselectivity (up to 21.3 normal–branched aldehyde) in the biphasic hydroformylation reaction [97].



69

Rhodium-catalyzed hydroformylation of alkenes (1-hexene, 1-octene, 1-nonene) in supercritical fluid–ionic liquid biphasic mixtures has been reported. Thus, the hydroformylation of 1-octene in a continuous flow process in which the substrate, gases and products are transported in and out of the reactor dissolved in supercritical carbon dioxide was studied using [Rh$_2$(OAc)$_4$] with [1-propyl-3-methylimidazolium]$_2$-[PhP(3-$C_6H_4SO_3$)$_2$] as the catalyst precursor dissolved in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate. Aldehydes (linear–branched = 3.8) were produced at a constant rate and selectivity for 72 h [98].

The effect of the nature of the cations and anions of a wide range of ionic liquids on the rhodium-catalyzed hydroformylation of 1-hexene (Rh(CO)$_2$(acac)/TPPMS 80 °C, 20 bar CO–H_2 = 1:1) has been studied. A correlation between the reaction rates and the solubility of 1-hexene in ionic liquids was found. The new phosphorus ligands **70**–**72** combined with Rh(CO)$_2$-(acac) were tested as catalyst precursors for hydroformylation of 1-hexene in ionic liquids. Using a mixture of tetrabutylammonium salt of the mono-, di- and trisulfonated triphenylphosphites **72** in the reaction up to 12.6 *n–i* ratio of the aldehyde products were observed [99].



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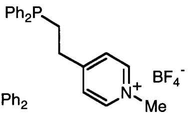

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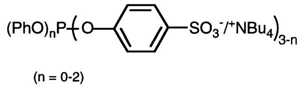
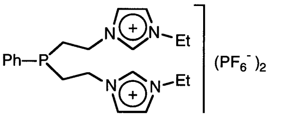


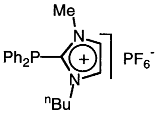
72

The cationic ligand **73** was tested in the rhodium-catalyzed biphasic hydroformylation of 1-octene using 1-butyl-3-methyl-imidazolium hexafluorophopsphate as the solvent of the catalyst. The in situ prepared catalyst $Rh(CO)_2(acac)$–**73** = 1:2 gave at 100 °C and 30 bar synthesis gas pressure ($CO–H_2 = 1:1$) a turnover frequency of 32 mol 1-octene per mol Rh and hour, and a *n–i* ratio of the aldehydes of 2.8 [100].



73

The ligands **74** and **75** have been tested in the biphasic rhodium-catalyzed hydroformylation of 1-octene employing the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate as the solvent of the catalyst. At 100 °C and 30 bar $CO–H_2 = 1:1$, 552 and 51 mol 1-octene per mol Rh per hour turnover frequencies were found with ligand **74** and **75**, respectively [101].



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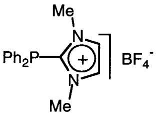
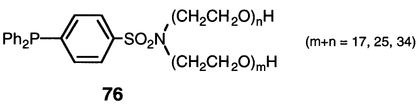


75

The influence of various parameters in the biphasic rhodium-catalyzed hydroformylation of 1-decene in the presence of chemically modified β-cyclodextrins was studied [102]. The role of β-cyclodextrin and dimethyl-β-cyclodextrin in the biphasic low-pressure hydroformylation reaction of $C_8–C_{16}$ akenes catalyzed by the water-soluble complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ was investigated. Recycling experiments have shown in four consecutive runs that each new run presents a slightly higher level of activity [103].

The rhodium complex of a new water-soluble phosphine **76** was found to exhibit high catalytic activity in the thermoregulated aqueous-organic biphasic hydroformylation of 1-decene [104].



76

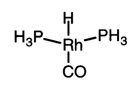
The hydroformylation of 4-octene has been realized in biphasic systems by the use of rhodium complexes of water-soluble calix[4]arene–phosphines [105].

See also Ref. [14].

1.3. Coordination chemistry related to hydroformylation

A theoretical study was made on the mechanisms of some elementary steps of the PH_3-modified cobalt-catalyzed olefin hydroformylation. All structural geometries of intermediates, transition states and products were optimized at the HF/LANL2DZ level under the effective core potential approximation. The activation energies of carbonyl insertion, H_2 oxidative addition and aldehyde reductive elimination were found to be 54, 134, and 43 kJ mol^{-1}, respectively [106].

A density functional theory study of the ethylene hydroformylation catalytic cycle employing a $HRh(PH_3)_2(CO)$ model catalyst was made. The potential energy hypersurface was mapped out at the CCSD(T)//B3LYP and B3LYP//B3LYP levels of theory. The preferred pathway for the catalytic cycle was found to originate from the *trans* isomer **77** of the active catalyst. The alternative pathway originating from the *cis* isomer of the active catalyst **78** were found to be less favorable owing to significantly higher barriers for the olefin insertion and CO insertion steps [107].



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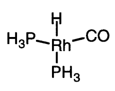
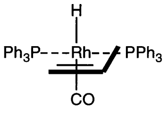


78

A hybrid QM/MM approach was employed to examine the regioselectivity of propene insertion into the Rh–H bond of $HRh(PPh_3)_2(CO)(\eta^2\text{-}CH_2{=}CHCH_3)$ in order to address the issue of kinetic versus thermodynamic control in hydroformylation. The calculations predict that two separate reaction pathways exist, one leading to the branched insertion product which is derived from the more active minor complex (**79**), and one leading to the linear insertion product which originates from the less active, major complex (**80**) [108].



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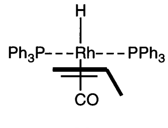


80

Considerations concerning the olefin migratory insertion into a metal–hydrogen or a metal–carbon bond were presented with particular reference to the work of the author in the field of hydrocarbonylation and olefin (co)polymerization reactions [109].

See also Refs. [37,45,46].

1.4. Engineering aspects of hydroformylation

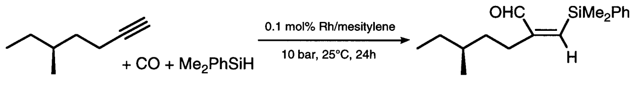
The dynamic behavior of an ideally stirred hydroformylation reactor has been described using a rigorous and an approximate model for the reaction [110].

An acoustic measurement technique was used to study the vapor–liquid critical points of the reaction mixtures of hydroformylation in carbon dioxide. The systems $CO_2 + CO + H_2 +$propene and $CO_2 + CO + H_2 + $1-hexene were investigated [111]. The critical temperatures and pressures were measured for a considerable number of mixtures representing the various stages of the hydroformylation reaction of propene in supercritical CO_2 and different reactant concentrations. Critical point data have also been measured for all of the binary mixtures of the components CO_2, H_2, CO, propene, *n*- and *iso*-butyraldehyde [112].

2. Hydroformylation related reactions of CO

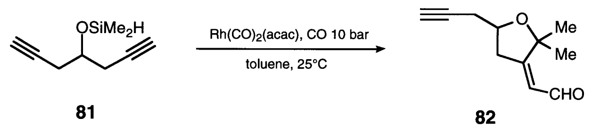
2.1. Silylformylation

The catalytic activity of mesitylene-solvated rhodium atoms in the silylformylation of acetylenes was investigated. (*Z*)-Silylalkenals was obtained in high yields (60–95%). The catalytic activity of the solvated rhodium in silylformylation was found to be comparable with and even higher than that of $Rh_4(CO)_{12}$. When optically active acetylenes were treated with hydrosilane under carbon monoxide pressure, the Rh/mesitylene-catalyzed silylformylation was found to give optically active β-silylalkenals with complete stereoselectivity [113]. E.g.:

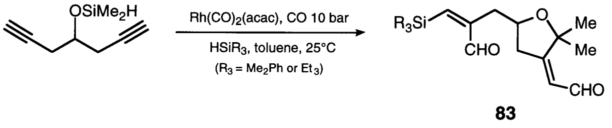


64% yield, 92% ee

Rhodium-catalyzed intramolecular silylformylation of **81** was found to afford 5-*exo*-(formylmethylene)-oxasilacyclopentanes (**82**) in 98% yield. In the presence of $HSiMe_2Ph$ or $HSiEt_3$ the reaction gives product **83** in quantitative yield [114].

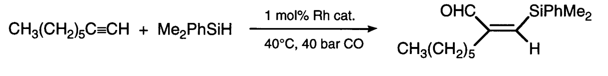


81 **82**



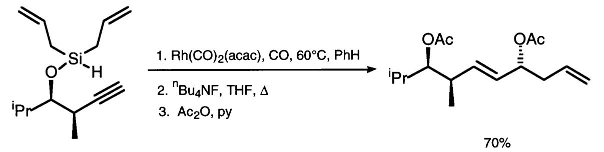
83

The zwitterionic rhodium complex $[Rh^+(CO)(\eta^6\text{-}C_6H_5BPh_3)^-]$ in 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid was found to catalyze the biphasic stereoselective silylformylation of 1-alkynes with Me_2PhSiH under either a CO or synthesis gas atmosphere with excellent catalyst recycling [115]. E.g.:

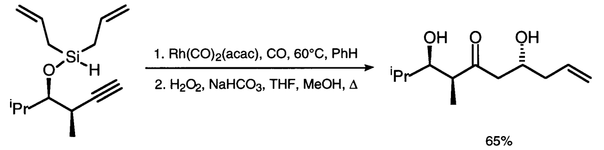


78% isolated yield

Tandem intramolecular alkyne silylformylation–allylsilylation was applied in the diastereoselective preparation of 1,5-diol derivatives [116]. E.g.:

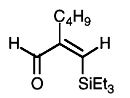


70%



65%

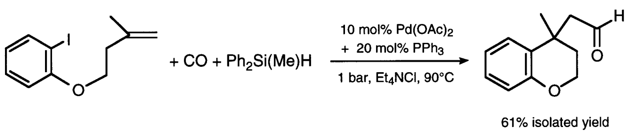
The complexes [Rh(COD)(L–L′)](BF_4), and [RhCl(CO)(L–L′)] (L–L′ = $P(bzN)Ph_2$, $P(bzN)_2Ph$, $P(bzN)_3$ (bzN = 2-(dimethylaminomethyl)phenyl), PePy, or $PePy_2$ ($PePy_n = P(CH_2CH_2Py)_nPh_{3-n}$; Py = 2-pyridyl; $n = 1, 2$) were found to be excellent catalysts for the silylformylation of 1-hexyne with triethylsilane in THF at atmospheric pressure and room temperature. Yields of **84** higher than 95% were obtained with some of the catalysts [117].

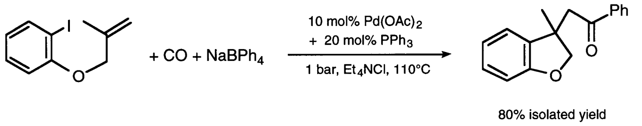


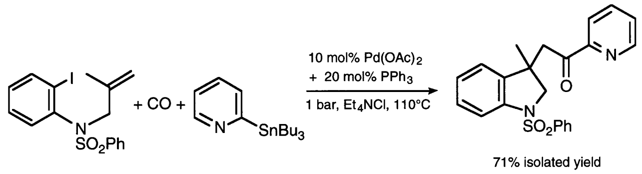
84

2.2. Cyclocarboformylation, alkoxycarbonylation, hydrocarboxylation, and thiocarbonylation

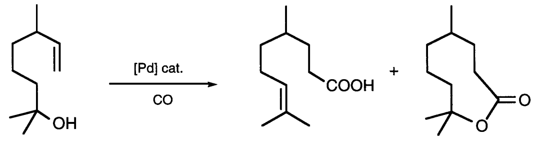
Interesting analogues of hydroformylation, namely the palladium-catalyzed cyclocarboformylation processes were found to provide a wide variety of products depending on the substrates and reagents [118]. E.g.:







Carbonylation of dihydromyrcenol (**85**) in the presence of $PdCl_2(PPh_3)_2$–$SnCl_2$–PPh_3 catalyst system in toluene was studied at 75 °C and 100 bar CO pressure. The main product was found to be the terminal carboxylic acid **86** in up to 92% yield. Under the same experimental conditions but in the presence of 4A molecular sieves, the lactone **87** was formed in $>93\%$ selectivity [119].



85 **86** **87**

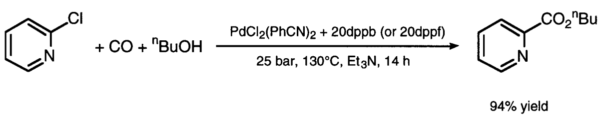
The Pd–TPPTS–HOTs catalyzed hydrocarboxylation of *N*-allylacetamide in aqueous medium was found to afford 4-acetamidobutyric acid and 3-acetamido-2-methylpropanoic acid under mild conditions, with a high regioselectivity towards the linear isomer (up to 29 linear–branched ratio) [120].

The poly(*N*-vinyl-2-pyrrolidone)-supported $PdCl_2$–$CuCl_2$–PPh_3 bimetallic catalyst system was used for the carbonylation of α-(6′-methoxy-2′-naphthyl)ethanol to the methyl ester of naproxen. Effects of temperature, CO pressure, reaction time and P–Pd ratio were studied in order to achieve optimum reaction conditions [121].

$PdCl_2L_2$-type complexes ($L = PPh_x(C_6F_5)_{3-x}$; $x = 0$–3, $P(OMe)_3$, $P(OPh)_3$, $P(OEt)_3$, $PPh_2(OC_6F_5)$, $PPh_2(O$-3,5-$F_2C_6H_3)$, $PPh_2(O^nBu)$, $PPh_2(O^tBu)$) were found to be active as precursors of benzyl bromide carbonylation catalysts at 40 °C and 1 bar CO in methanol in the presence of triethylamine. The highest yield of the carbonylation product (92%), phenylacetic acid methyl ester, was obtained using *cis*-$PdCl_2[P(OMe)_3]_2$ [122].

Palladium-catalyzed single and double carbonylation of aryl halides in 1-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate has been reported. It was found that the use of these ionic liquids as the reaction media significantly enhances the reactivity of the carbonylation reactions, and that the catalyst–ionic liquid mixture can be recycled after separation of the product [123].

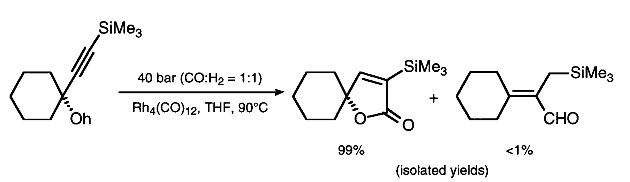
The palladium/diphosphine-catalyzed alkoxycarbonylation of various *N*-heteroaryl chlorides was examined. Among the different ligands tested, 1,4-bis(diphenylphosphino)butane and 1,1′-bis(diphenylphosphino)ferrocene were found to lead to the most efficient palladium catalyst systems for the conversion of 2-chloropyridines and similar heteroaryl chlorides into the corresponding butoxyesters [124]. E.g.:



2,3-Dichloropyridines were found to undergo a mono- or a dicarbonylation in the presence of carbon monoxide, an alcohol, and a palladium catalyst, affording selectively either alkyl 3-chloropyridine-2-carboxylates or dialkyl pyridine-2,3-dicarboxylates in good yields, depending on the reaction conditions. For instance, the process could be scaled up for the monoalkoxycarbonylation of 2,3-dichloro-5-(trifluoromethyl)pyridine, affording in high yield and selectivity the corresponding 3-chloro-5-(trifluoromethyl)pyridine-2-carboxylate [125].

Photoalkoxycarbonylation of β-pinene and of other alkenes was achieved in a methanol–acetone = 3:1 solvent mixture at 14 °C containing $Co(acac)_2$ as the precatalyst. A tentative catalytic cycle involving anionic cobalt carbonyl intermediates was suggested [126].

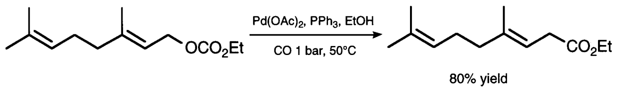
3-Silyl-2(5*H*)-furanones were found to be readily and selectively formed in the $Rh_4(CO)_{12}$-catalyzed carbonylation of propargyl alcohol derivatives bearing a trialkylsilyl group on the terminal sp-carbon under hydroformylation conditions [127]. E.g.:

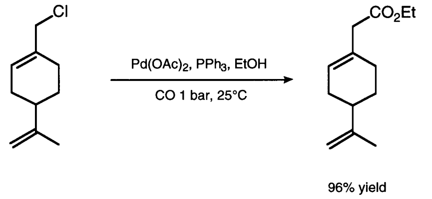


The regioselective catalytic hydroalkoxycarbonylation of alkenes with carbon monoxide and alcohols in the presence of the system $PdCl_2$–PPh_3–*p*-TsOH was studied [128,129].

The effect of water, dihydrogen, and *p*-toluenesulfonic acid on the hydroesterification of ethylene to methylpropionate using a $Pd(PPh_3)_2(OTs)_2$ catalyst precursor has been investigated. Based on the observed promoting effect of the hydride sources the insertion of the olefin into a Pd–H species seems to be the initial step of the catalytic cycle [130].

Palladium-catalyzed alkoxycarbonylations of terpenic allylic carbonates and chlorides were found to proceed highly selectively under mild conditions to afford β,γ-unsaturated esters [131]. E.g.:

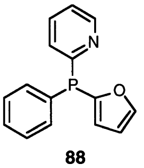




The diastereoselective hydroalkoxycarbonylation of terpenes (limonene, carvone, dihydrocarvene, pulegone) and vinylestrone has been studied using chiral and achiral palladium–phosphine catalysts [132]. The catalytic pathways of the $Pd(PPh_3)_2Cl_2$ and $Pd(PPh_3)_2$–$SnCl_2$ catalyzed 1-hexene hydroalkoxycarbonylation reaction have been elucidated by using deuterium labeling. The labeled species in residual olefins and carbonylated products support the assumption that the palladium hydride route is operating in the mechanism of this system. It was found that alkyl–metal intermediates undergo reversible β-hydride elimination even at low reaction temperature [133,134].

A palladium-catalyzed asymmetric bis(alkoxycarbonylation) reaction of terminal olefins in the presence of copper(I) triflate was achieved by using a chiral bioxazoline ligand, (4*S*,4′*S*)-4,4″-dibenzyl-4,4′,5,5′-tetrahydro-2,2′-bioxatole, under normal pressure of carbon monoxide and dioxygen at 25 °C to give the corresponding optically active monosubstituted succinates with enantioselectivities up to 66% ee [135].

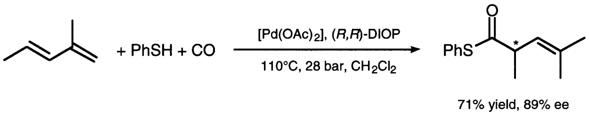
Iminophosphine–palladium(0) complexes in the presence of methanesulfonic acid were investigated as catalysts for the methoxycarbonylation of phenylacetylene. The efficiency of this system was found to be low [136]. (2-Furyl)phenyl(2-pyridyl)phosphine (**88**) in combination with $Pd(OAc)_2$ and methanesulfonic acid was found to be highly active in the regioselective methoxycarbonylation of phenylacetylene [137].



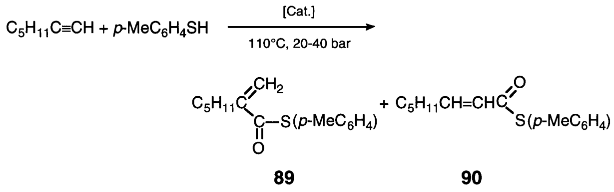
88

A corrigendum to "Stereoselective synthesis of substituted ketopyranose subunits of polyketide natural products by intramolecular alkoxycarbonylation of δ-alkynyl alcohols" Tetrahedron Lett. 41 (2000) 4717–4721 has appeared [138].

Asymmetric thiocarbonylation of prochiral 1,3-conjugated dienes with thiophenol and CO for the synthesis of optically active β,γ-unsaturated thiol esters has been developed by using a catalyst system based on $[Pd(OAc)_2]$/(*R*,*R*-DIOP) at 110 °C and 28 bar CO pressure in methylene chloride [139]. E.g.:



The regioselectivity of the thiocarbonylation of terminal acetylenes with arylthiols catalyzed by palladium(II) and diphosphine ligands was investigated. The catalytic system $Pd(OAc)_2$–dppp–CO–*p*-TsOH–THF was found to afford the thioester **89** as the main product (87%), whereas the catalytic system $PdCl_2$–dppb–CO + $5H_2$–CH_2Cl_2 gave the thioester **90** as the main product (75%) [140].



See also Ref. [143].

2.3. Amidocarbonylation and hydroaminomethylation

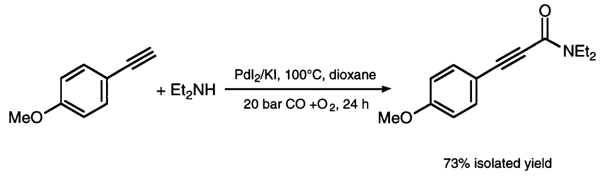
The ruthenium-catalyzed carbonylation of cyclic secondary amines has been studied using in situ infrared spectroscopy and a tentative catalytic cycle was suggested [141].

The amidocarbonylation of cyclohexene and 1-pentene catalyzed by trialkylstibines-modified $Co_2(CO)_8$ was investigated. The best results, up to 80% yield of the *N*-acyl aminoacid, were obtained at 120 °C and 28 bar CO–$H_2 = 3{:}1$ using tri(*o*-tolyl)stibine or tri(*p*-fluorophenyl)stibine as the modifier [142].

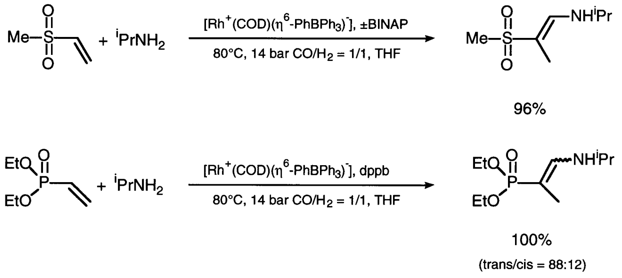
The rhodium-catalyzed hydroaminomethylation and the palladium-catalyzed alkoxycarbonylation of Δ^{16}-steroids were studied in order to obtain new 16-α-aminomethyl derivatives and 16-α-ester derivatives, respectively [143]. The hydroaminomethylation of arylethylenes was studied using the zwitterionic rhodium complex $[Rh^+(COD)(\eta^6\text{-}PhBPh_3)^-]$ as the catalyst. Hydroaminomethylation of styrene under relatively mild conditions (80 °C, 14 bar CO–$H_2 = 1{:}1$) in the presence of isopropylamine in 85% isolated yield, with the linear isomer as a by-product (branched–linear ratio = 11.5) [144].

Supercritical carbon dioxide was found to act simultaneously as solvent and temporary protecting group during homogeneous rhodium-catalyzed hydroaminomethylation of ethyl methallylic amine. Cyclic amines are formed as the major products in supercritical carbon dioxide, whereas the cyclic amide is formed preferentially in conventional solvents [145].

Palladium iodide/KI-catalyzed oxidative aminocarbonylation of 1-alkynes was found to occur at 100 °C and under 20 bar of a 4:1 mixture of CO and air [146]. E.g.:



The zwitterionic rhodium complex $[Rh^+(COD)(\eta^6\text{-}PhBPh_3)^-]$ in the presence of an appropriate phosphine was found to catalyze the novel hydroaminovinylation reaction of vinylsulfones and a vinylphosphonate [147]. E.g.:



See also Ref. [85].

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

Proton transfer between H_2O and $FeH(CO)_4^-$, the assumed slow step of the water–gas shift reaction catalyzed by $Fe(CO)_5$, has been studied by Hartree–Fock and multiconfiguration CASSCF ab initio methods [148].

Pretreating ruthenium(bipyridine) carbonyl complexes on silica with sodium carbonate/methanol solution under CO atmosphere was found to afford highly effective catalysts for low-temperature (100–150 °C) heterogeneous water–gas shift reaction. The most active catalyst proved to be Na_2CO_3-activated dimeric $[Ru(bpy)(CO)_2Cl]_2$ with a turnover frequency as high as 17 000 mol product/mol Ru/24 h at 150 °C [149].

2.5. Reduction of CO and CO_2

The electrocatalytic reduction of CO_2 in the presence of nickel(II) complex of 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1]octadecane was studied using cyclic voltametry and controlled-potential electrolysis techniques. Carbon monoxide was found to be the major product in the gaseous phase and formic acid the sole product formed in the solution phase [150].

Simultaneous electrochemical reduction of carbon monoxide and nitrite ions was investigated at gas-diffusion electrodes with various metallophthalocyanines (Cr, Mo, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, In, Tl, Sn, Pb) as the catalysts [151].

Electrochemical synthesis of carboxylic acids from CO_2 and alkenes (propene, 1-butene and 1,3-butadiene) using various nickel-organic mediators has been studied [152].

The kinetics of CO_2 hydrogenation to formic acid catalyzed by $RuCl(O_2CCH_3)P(CH_3)_3$ in liquid triethylamine at subcritical CO_2 pressures were studied. The reaction was found to be first-order in both H_2 and CO_2 under most conditions, which support a CO_2 insertion mechanism [153].

Nickel tetracarbonyl promoted by methoxy ion was found to effect the facile conversion of synthesis gas into methanol. At 100 °C, syngas conversion of 99% with a turnover frequency of 66 h^{-1} was observed. The kinetics of the $Ni(CO)_4$–KOMe catalyst system in 1,2-bis(2-methoxyethoxy)ethane(triglyme)–MeOH solvent mixture have been studied [154].

Nickel(II) complexes with derivatives of 1,4,8,11-tetraazacyclotetradecane incorporated into a bicontinuous cubic liquid-crystalline layer modifying the thin mercury film or glassy carbon electrode were found to be active in catalytic reduction of carbon dioxide. The linear dependence of catalytic reduction current on the concentration of carbon dioxide allowed the use of the system for carbon dioxide sensing in the solution [155]. The electrochemical reduction of carbon dioxide in the presence of hexa–aza–macrocycle complexes of zinc(II) and nickel(II) as catalysts was investigated [156].

An erratum to “The effect of weak Brönsted acids on the electrocatalytic reduction of carbon dioxide by a rhenium tricarbonyl bipyridyl complex” [J. Electroanal. Chem. 453 (1998) 161–170] has appeared [157].

3. Reviews

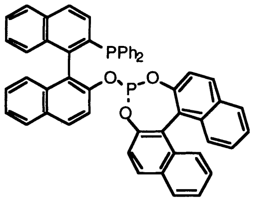
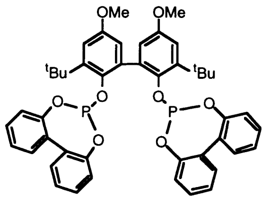
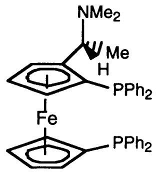
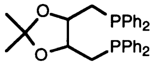
1) *Rhodium catalysed hydroformylation*. A multi-chapter monograph about the state of the art in rhodium catalyzed hydroformylation covering among others the unmodified, phosphite- and phosphine-modified catalysts, asymmetric hydroformylation, and biphasic hydroformylation. No references [158].
2) *Wide bite angle diphosphines: Xantphos ligands in transition metal complexes and catalysis*. A review about the development and application of XANTHPHOS-type ligands with bite angles of 100–134° among others in rhodium- and platinum-catalyzes hydroformylation with more than 49 references [159].

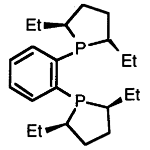
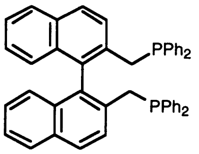
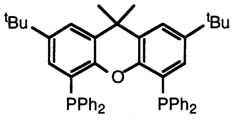
3) *On the mechanism of the hydroxycarbonylation of styrene with palladium systems*. A review with 127 references [160].
4) *Kinetic modeling of homogeneous catalytic processes*. The kinetic modeling of various catalytic carbonylation reactions has been reviewed with 60 references [161].
5) *Decomposition pathways of homogeneous catalysts*. A review with examples of catalyst decomposition of commercial interest, among others in hydroformylation, with 109 references [162].
6) *Bite angle effects in hydroformylation catalysis*. A review with 32 references [163].
7) *Recent advances in homogeneous catalysis using platinum complexes*. A review of recent examples among others of hydroformylation reactions that can be effectively catalyzed by platinum complexes, with more than 64 references [164].
8) *The use of supercritical fluids in synthetic organic chemistry, among others in hydroformylation* has been reviewed with 11 references [165].
9) *Transition metal catalysis using functionalized dendrimers*. A review about the recent progress made with novel transition metal functionalized dendrimers that are used as catalysts among others in hydroformylation reactions with more than 84 references [166].
10) *Recent advances on chemo-, regio- and stereoselective hydroformylation*. A review with more than 171 references [167].
11) *Dendritic catalysts and dendrimers in catalysis*. A review with 255 references among others in connection with hydroformylation [168].
12) *Solid-phase dendrimer chemistry: synthesis and applications*. A review with 57 references [169].
13) *Palladium-catalyzed Reppe carbonylation*. A comprehensive review of the homogeneous palladium-catalyzed reaction of an unsaturated hydrocarbon substrate, a carbonyl source and a nucleophile, covering reactivity patterns, side reactions, catalyst chemistry, mechanism, and industrial aspects with 296 references [170].

Acknowledgements

The author thanks the Hungarian Science Fund for support under Grant No. OTKA 25028.

Appendix A

Ac	acetyl
acac	acetylacetonate
Ar	aryl
BDPP	2,4-bis(diphenylphosphino)pentane
BINAP	2′,2′-bis(diphenylphosphino)-1,1′-binaphthyl
BINAPHOS	
BIPHEPHOS	
Bn	benzyl
BPPFA	
bpy	2,2′-bipyridine
Bu	butyl
CHIRAPHOS	2,3-bis(diphenylphosphino)butane
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cy	cyclohexyl
DIOP	2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane 
DMA	*N*,*N*-dimethylacetamide
DMF	*N*,*N*-dimethylformamide
DMSO	dimethylsulfoxide
dppb	$Ph_2PCH_2CH_2CH_2CH_2PPh_2$
dppe	$Ph_2PCH_2CH_2PPh_2$

dppf	1,1′-bis(diphenylphosphino)ferrocene
dppp	$Ph_2PCH_2CH_2CH_2PPh_2$
ee	enantiomer excess
Et	ethyl
Et-DuPHOS	
IR	infrared
Me	methyl
NBD	norbornadiene
NAPHOS	2,2′-bis(diphenylphosphanylmethyl)-1,1′-binaphthyl 
Ph	phenyl
py	pyridine
sc	supercritical
THF	tetrahydrofuran
Tf	triflate (trifluoroacetyl)
TN	turnover number (mol product/mol cat)
TOF	turnover frequency (mol product/mol cat/time)
TPPDS	disodium salt of the disulfonated triphenylphosphine
TPPMS	sodium-*m*-(diphenylphosphino)benzene sulfonate
TPPTS	trisodium salt of the trisulfonated triphenylphosphine
Ts	tosyl (*p*-toluenesulfonyl)
TsOH	*p*-toluenesulfonic acid
XANTPHOS	

Appendix B: The metals and their associated references

Metal	References
Zr	[77,78]
Cr	[35,151]
Mo	[35,151]
W	[35]
Mn	[66,151]
Re	[66]
Fe	[148]
Ru	[4,67,75,141,149,151,153,157]
Co	[1–3,68,75,106,109,126,142,151]
Rh	[5–66,71,73,76–105,107–109,113–117,127,143–147,151,158,159,163,168,169]
Ni	[150–152,154–156]
Pd	[68,69,118–125,128–140,143,146,151,160,161,170]
Pt	[14,70–74,151,164]
Cu	[121,135,151]
Ag	[151]
Au	[151]
Zn	[28,151,156]
Cd	[151]
In	[151]
Tl	[151]
Sn	[14,70,72–74,119,151]
Pb	[151]

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