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Review

Application of transition metals in hydroformylation annual survey covering the year 2003

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Contents

Abstract

Hydroformylation in homogeneous and heterogeneous systems, and hydroformylation related reactions of carbon monoxide reported in 2003 are reviewed.

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

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1. Hydroformylation

1.1. Homogeneous systems

1.1.1. Cobalt catalysts

Tertiary phosphine ligands derived from (*R*)-(+)-limonene (**1**) were used in cobalt-catalyzed 1-dodecene hydroformylation at 170 °C under 85 bar syngas (H_2:CO = 2:1) with a

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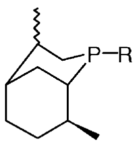
cobalt concentration of 1000 ppm and a phosphine to cobalt ratio of 2:1 in a C9–C11 paraffin mixture as the solvent. The activity and selectivity was found to be governed by the equilibria between the modified and unmodified cobalt catalytic species in the reaction. The observed *n*:*iso* ratio of the product ranged from 2.6 to 4.9. Hydrogenation of 1-dodecene was 5–6% [1].



R = *n*-$C_{18}H_{37}$, *n*-$C_{10}H_{21}$, *n*-C_5H_{11}, *n*-C_4H_9, $(CH_2)_3Ph$, $(CH_2)_3CN$, $(CH_2)_3OCH_2Ph$, $(CH_2)_2OCH_2CH_3$

1

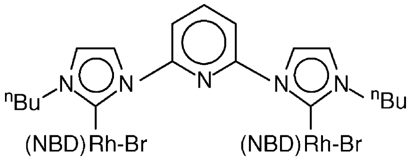
1.1.2. Rhodium catalysts

The homogeneous catalytic hydroformylation of 3,3-dimethyl-1-butene using $Rh_4(CO)_{12}$ as the catalyst precursor was studied by in situ FTIR spectroscopy and band-target entropy minimization. The pure component spectra of the main species present, 3,3-dimethyl-1-butene, 4,4-dimethylpentanal, $Rh_4(CO)_{12}$, and $C_6H_{13}C(=O)Rh(CO)_4$ were recovered. The pure component spectra of the expected minor species, 2-methyl-3,3-dimethylbutanal, $Rh_6(CO)_{16}$, and $Rh_4(\sigma\text{-}CO)_{12}$ were recovered as well [2]. Using minimization of entropy and spectral similarity to recover pure component spectra from in situ experimental FTIR spectral data was successfully applied to reconstruct spectra of unknown intermediate products as well in the case of the homogeneous rhodium-catalyzed hydroformylation of isoprene [3]. High-pressure in situ FTIR and polymer matrix techniques was used to study the rhodium-catalyzed hydroformylation of 1-octene, 1-butene, propene, and ethene using $Rh(acac)(CO)_2$ or $Rh(acac)(CO)(PPh_3)$ in a polyethylene matrix as the catalyst precursor. The acyl rhodium intermediates, $RC(=O)Rh(CO)_4$ and $RC(=O)Rh(CO)_3(PPh_3)$ were observed. It was found that the acyl rhodium tetracarbonyl intermediates easily react with ethene to form acyl rhodium tricarbonyl species $RC(=O)Rh(CO)_3(C_2H_4)$ [4].

An additional gas such as dinitrogen, argon or xenon, present in the reaction medium in high concentration was found to decrease the rate of hydroformylation of cyclohexene, 1-hexene or styrene in the presence of $RhH(CO)(PPh_3)$. This effect was attributed to a competition between the additional gas and one of the reagents, alkene, dihydrogen or carbon monoxide for a coordinative unsaturated site available on the catalytically active intermediates [5].

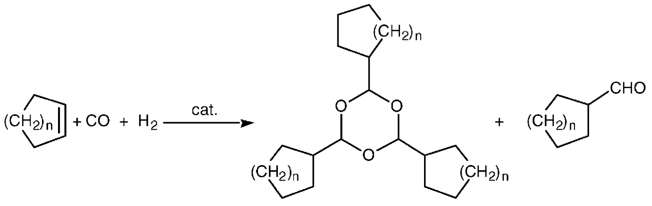
Carboalkoxyrhodium complexes as the dormant states of rhodium hydroformylation catalysts were recognized by in situ high-pressure FTIR spectroscopy if the alkene feed contained enones [6]. The rhodium-catalyzed hydroformylation of 1-hexene and styrene using the alkoxycarbonylcyclopentadienyl rhodium(I) complexes $[Rh\{C_5H_4CO_2X\}(L,L)]$ $[X = -CH_2CH = CH_2, -(CHR)_2OH$ (R = H, Me); L,L = 2CO, NBD] as the catalyst precursors was studied and compared with the unsubstituted system $[Rh(C_5H_5)NBD]$ [7].

A new dirhodium(I) bisimidazolium–carbene complex (**2**) was used as catalyst precursor in hydroformylation of vinylarenes, 1-octene, and 2,5-dihydrofuran giving high selectivities for the branched aldehyde isomer (up to 100% at 25 °C and 30 bar CO:H_2 pressure) when vinylarenes were used as substrates. High-pressure NMR spectroscopy provided evidence that the dinuclear unit containing the carbene ligand is maintained under catalytic conditions [8].



2

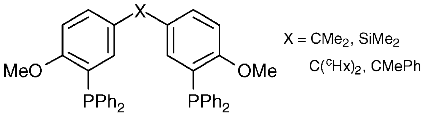
The one pot hydroformylation-cyclotrimerization reaction of cyclopentene and cyclohexene was found to be catalyzed by $Rh_6(CO)_{16}$ and $H_3PW_{12}O_{40}{\cdot}xH_2O$ in THF at 100 °C and 40 bar CO:H_2 = 1:1 to give 2,4,6-trisubstituted-1,3,5-trioxanes (**3**) as major products along with the corresponding aldehydes (**4**) [9].



n = 1,2 **3** **4**

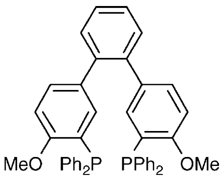
The effect of phosphorus ligands and reaction conditions on the diastereoselectivity in the rhodium-catalyzed hydroformylation of β-pinene and camphene was studied [10]. Hydroformylation of 1,4-diacetoxy-butene using homogeneous $HRh(CO)(PPh_3)_3$ catalyst, on Na–Y zeolite support tethered Rh-complex catalyst, and a water-soluble Rh-TPPTS catalyst in a two-phase system was studied. It was found that both the tethered and biphasic catalysts were highly stable during recycle, though the activity of these catalysts was lower than that of the homogeneous catalyst [11].

Several *o*-substituted arylphosphine ligands, such as (2-cyclohexylphenyl)diphenylphosphine, (2-isopropylphenyl)diphenylphosphine, (2-methylnaphthyl)diphenylphosphine were tested in the rhodium-catalyzed hydroformylation of propene and 1-hexene. It was found that the increasing size of the *o*-alkyl-substituent effects favorably the *iso*-selectivity [12]. New diphosphine ligands 5 and 6 were tested in rhodium-catalyzed hydroformylation of 1-octene. Especially with ligand 6 high activities (TOF = 3485 mol 1-octene/mol Rh h^{-1} at 80 °C and 20 bar, ligand:Rh = 6:1, 1-octene:Rh = 4000:1) were obtained [13].



X = CMe_2, $SiMe_2$
$C(^cHx)_2$, CMePh

5



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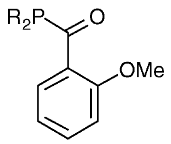
Hydroformylation of 1-hexene using new phosphomide ligands 7 and $Rh(acac)(CO)_2$ as the catalyst precursor was investigated at 60 °C and 20 bar $CO:H_2 = 1$ [14].

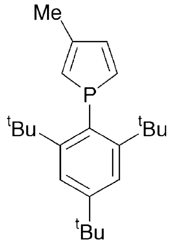


R = Ph, CH_2CH_2CN, ^cHx

7

Highly selective (95%) tandem isomerization-hydroformylation reaction of *trans*-4-octene to *n*-nonanal was found by using the $Rh(acac)(CO)_2$-BIPHEPHOS catalytic system in propylene carbonate solution at 125 °C and 20 bar syngas pressure [15]. Rhodium(I) complexes of upper rim 1,2- and 1,3-diphosphinated calix[4]arenes have been tested as catalysts in hydroformylation of 1-hexene, styrene, vinyl acetate, vinyl benzoate, and vinyl *p-tert*-butylbenzoate [16]. Rhodium complexes of bidentate phosphorus ligands assembled on a dimeric zinc(II) porphyrin template from functionalized monomeric ligands were tested in the hydroformylation reaction of 1-octene and styrene. Enhanced selectivities were observed compared to the non-template analogue [17]. Rhodium(I)-catalyzed ($Rh(acac)(CO)_2$, XANTHPHOS, 70 °C, 20 bar $CO:H_2 = 1$) regioselective hydroformylation of aromatic diallyl ethers of hydroquinone, 2,2′-biphenol, and 1,1′-bi-2-naphthol gave the corresponding dialdehydes in up to 80% yield. Subsequent reductive amination of the dialdehydes in the presence of α,ω-diamines using the same catalyst but 40–50 bar H_2 pressure led to azamacrocyclic rings in up to 71% yield. Bis-methylallyl ethers of hydroquinone, 2,2′-biphenol, and 1,1′-bi-2-naphthol and α,ω-diamines could be converted into the corresponding azamacrocycles in one step at 80 °C and 80 bar $CO:H_2 = 1:1$ pressure using $Rh(acac)(CO)_2$ as the catalyst precursor [18].

High chemoselectivities towards hydroformylation and high regioselectivities towards the branched aldehyde isomer were obtained in the hydroformylation of styrene at 40 °C and 50 bar $CO:H_2 = 1:1$ in the presence of an in situ rhodium catalyst containing sterically hindered 1-arylphosphole ligands **8**–**14** [19].



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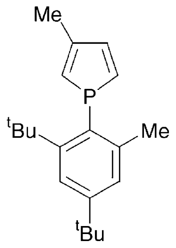

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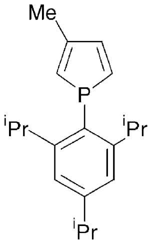

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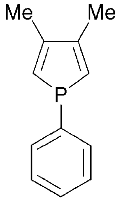

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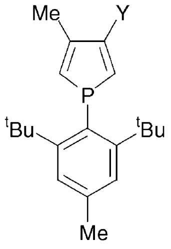

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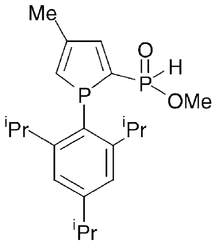

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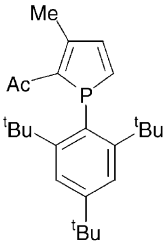

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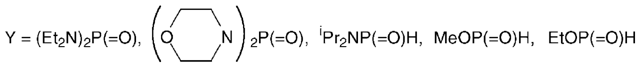
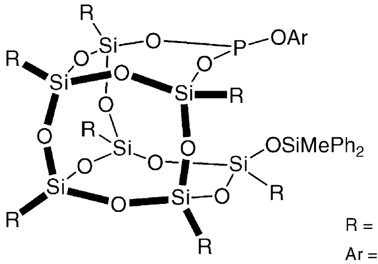

Y = $(Et_2N)_2P(=O)$, $_2P(=O)$, $^iPr_2NP(=O)H$, MeOP(=O)H, EtOP(=O)H

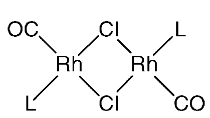
High activities with turnover frequencies of up to 5000 h^{-1} at 80 °C were obtained in the rhodium(I)-catalyzed hydroformylation of 1-octene modified by nanostructured silsesquioxane-based monophosphite compounds (14) named POSSphites [20].



R = cyclopentyl;
Ar = phenyl, 3,5-di-*tert*-butylphenyl, 1-naphthyl

14

Aminophosphonite-phosphite and aminophosphonite-phosphinite chiral ligands have been tested in rhodium(I)-catalyzed asymmetric hydroformylation of vinyl acetate. At 60 °C, regioselectivities higher than 98% were obtained, but the enantioselectivities were only up to 32% ee [21]. The rhodium(I) complex 15 with the ligand 16 was found to be active as a catalyst precursor in the hydroformylation of styrene, yielding initial turnover frequencies up to 440 h^{-1} and selectivities up to 74% in the branched aldehyde at 80 and 60 °C, respectively. No enantiomeric excesses were observed [22].



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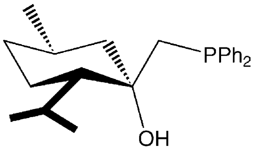
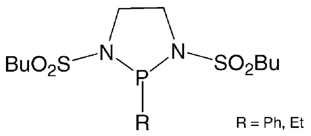


16

Asymmetric hydroformylation of styrene, 2-vinylnaphthalene, 1-hexene, vinyl acetate, indene, (*Z*)-2-butene, and methyl *N*-acetamidoacrylate was examined using Rh(acac) complexes of BINAPHOS, 3-MeO-BINAPHOS, and 3-^{i}PrO-BINAPHOS as catalyst precursors. For all the olefins, the *iso*-selectivity and the % ee values were found to be higher using MeO- or ^{i}PrO-substituted BINAPHOS compared to those obtained using BINAPHOS [23].

A new concept for the construction of bidentate ligands employing self-assembly of two monodentate ligands through hydrogen bonding was used to obtain highly active and highly regioselective catalysts for the *n*-selective hydroformylation of terminal alkenes. Thus, a catalytic system composed of Rh:6-diphenylphosphanyl-2-pyridone:1-octene = 1:20:7000, [1-octene] = 1.4 M was found to give at 65 °C and 10 bar CO:H_2 = 1:1 in toluene 56% conversion in 4 h and a linear: branched aldehyde ratio of 97:3 [24].

Mono- and bidentate sulfonylaminophosphines **17** and **18** were tested as ligands in rhodium(I)-catalyzed hydroformylation of 1-hexene at 60 and 80 °C and 4–11 bar CO:H_2 = 1:1 pressure in THF, toluene, CH_2Cl_2, and dioxane. It was found that the highest ratios of linear to branched aldehydes were obtained with the monodentate ligands (*n*:*iso* > 10) while the bidentate alkanesulfonamide 18 gave a lower *n*:*iso* ratio of 7.2 but the highest rate (TOF = 1130 mol aldehyde/mol Rh h^{-1}) [25].



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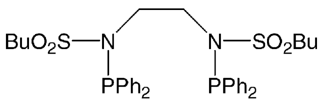
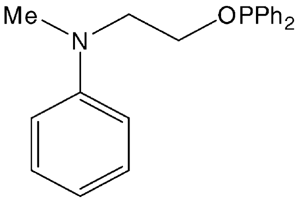


18

A new supramolecular approach was used to obtain chelating bidentate phosphite ligands for regioselective rhodium-catalyzed hydroformylation. The self-organizing multicomponent assembly consists of two (zinc(II) porphyrin)phosphite and three 1,4-diazabicyclo[2.2.2]octane, which coordinates rigidly to a Rh(acac)-part as a chelate. The rhodium catalyst based on such an assembly was studied in the rhodium-catalyzed hydroformylation of 1-octene. Very high activity and a linear to branched ratio of 15.1 was found at 80 °C [26]. The direct introduction of formyl groups into β-vinyl-metalloporphyrins via a PPh_3-modified rhodium-catalyzed hydroformylation reaction has been described. The regioselectivity of the reaction was found to be remarkably dependent on the metal centre of the porphyrin, yielding 100% of the branched aldehyde with zinc(II) complexes and 75% with the nickel(II) one [27].

Terminal alkenes anchored on a polymer were hydroformylated at 40 °C with 20 bar CO:H_2 = 1 using solutions of phosphine-modified rhodium complexes as the catalysts [28,29]. New nitrogen-containing phosphinite **19** and phosphine–phosphinite **20** ligands were tested as ligands in rhodium-catalyzed styrene hydroformylation. Moderate to good catalytic activity was found under mild reaction conditions [30].



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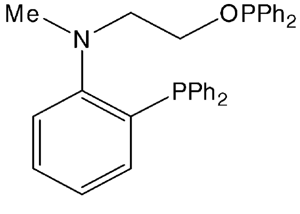
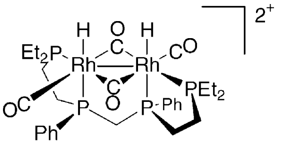


20

Hydroformylation and hydroaminomethylation of 1-octene was studied using cationic rhodium complexes as the catalysts. The complexes $[(H_2C(3,5\text{-}Me_2pz)_2Rh(CO)L]BF_4$ (L = CO, $P(OMe)_3$, PPh_3, $PMePh_2$, pz = pyrazolyl) were found to be active in the hydroformylation and in the hydroaminomethylation reaction of 1-octene at 80 °C and 12 bar CO:H_2 = 1:1 pressure [31]. A series of phenoxaphosphine- and dibenzophosphole-modified XANTPHOS-type ligands were used for the rhodium-catalyzed hydroformylation of terminal and internal olefins. The effect of natural bite angle on hydroformylation activity and selectivity was investigated [32]. Carbosilane dendrimers with XANTPHOS-type ligands located in the core were used as ligands in rhodium-catalyzed 1-octene hydroformylation [33].

Rhodium(I) complexes with chiral phosphite ligands based on chiral binaphthol were found to be efficient catalysts for the asymmetric hydroformylation of styrene and vinyl acetate. Good chemo- and regioselectivities but only mediocre enantioselectivities were achieved [34].

The addition of 30% water by volume to acetone was found to create a simple polar-phase solvent system that produces 30–115% rate enhancements for the hydroformylation of 1-hexene with a variety of monometallic rhodium phosphine catalysts, and a 265% rate increase for a dirhodium tetraphosphine catalyst 21 along with improved chemoselectivity to aldehyde products [35].



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Novel chiral diazaphospholidines—accessible by phosphorylating commercially available (*S*)-1,1′binaphthyl-2,2′-diamine—were tested in the rhodium-catalyzed asymmetric hydroformylation reactions. In the best case, 31% ee was achieved [36].

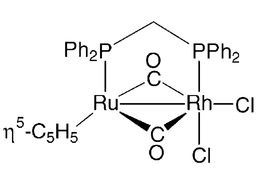
7-Formyl-5-methyl-5,6-dihydroindolizine and 7-formyl-6-methyl-5,6-dihydroindolizine were obtained via a rhodium complex-catalyzed domino hydroformylation–cyclization–dehydration reaction sequence starting from the corresponding 1-allyl-2-formylpyrroles [37]. A novel rhodium-catalyzed one-pot synthesis of indole systems via tandem hydroformylation-Fischer indole synthesis starting from olefins and arylhydrazines was described. The procedure leads directly to 3-substituted indoles if unsubstituted phenylhydrazine is used. Using *para-* or *ortho*-substituted arylhydrazines, the corresponding 3,5- and 3,7-disubstituted indoles are formed, respectively [38]. The rhodium-catalyzed diastereoselective hydroformylation of 2-substituted secondary alcohol *ortho*-diphenylphosphanylbenzoyl esters were examined. It was found that the diastereoselectivity increased as a function of the steric demand of the substituents both at the sterogenic center and in the alkene 2-position [39]. Five- and six-membered cyclic amino acids were prepared in good yield with high enantiomeric excess (>95%) via tandem rhodium-Et-DuPHOS-catalyzed asymmetric hydrogenation followed by a rhodium-catalyzed hydroformylation cyclization sequence in a single pot [40]. The rhodium-catalyzed asymmetric hydroformylation of crotono nitrile and allyl cyanide was investigated [41].

See also Refs. [45,49,50,52,68].

1.1.3. *Other metals as catalysts and bimetallic catalysts*

Dichlorotris(triphenylphosphine)ruthenium(II)-catalyzed liquid phase hydroformylation of propene in ethanol at 175 °C and 9 bar ($P(\mathrm{CO}) = P(\mathrm{H_2}) = P(\mathrm{propene}) = 3$ bar) pressure was investigated [42]. Ruthenium carbonyl compounds were found to be suitable catalysts for the hydroformylation of alkenes using CO_2 as the source of CO along with H_2. In the multi-step process, the CO_2 is first reduced to CO and then used in situ in hydroformylation. The best results were obtained by using a $[Ru(CO)_3Cl_2]_2/Li_2CO_3$ system [43].

The homogeneous hydroformylation of 1-octene using either of the heterobimetallic complexes 22 or 23 as catalysts were studied. The best results were obtained with complex 23, which showed the highest regioselectivity for the linear aldehyde [44].



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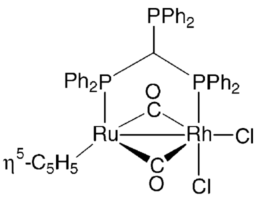

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The triangular early-late heterobimetallic $ZrRh_2$ complex $[Cp^{tt}_2Zr(\mu3{-}S)_2\{Rh(CO)_2\}_2]$ ($Cp^{tt} = \eta^5$-1,3-di-*tert*-butylcyclopentadienyl) in the presence of P-donor ligands was found to be a suitable catalyst precursor for the hydroformylation of 1-octene under mild conditions of pressure and temperature (7 bar $CO{:}H_2 = 1{:}1$, 80 °C). No Zr–Rh synergic effect was observed. The precursor breaks down after catalysis [45]. The catalytic activity of the heterotetranuclear $TiRh_3$ complex $[CpTi(\mu_3\text{-}S)_3\{Rh(CO)(PPh_3)\}_3]$ towards 1-hexene and styrene hydroformylation was investigated at 80 °C and 5 bar $CO{:}H_2 = 1{:}1$ [46].

The addition of manganese carbonyl hydride to the reaction mixture of the unmodified rhodium-catalyzed hydroformylation of 3,3-dimethyl-1-butene was found to lead to a significant increase in system activity. Based on in situ spectroscopic information this increase in rate of product formation was correlated with bimetallic catalytic binuclear elimination [47].

The hydroformylation reaction of 1-hexene was studied in the presence of iridium complexes as catalyst precursors and inorganic salts as promoters. The activity of the iridium compounds was found to increase in the order $IrCl_3 < [IrCl(CO)_3]_n < Ir_4(CO)_{12}$. The use of promoters such as LiCl, Li_2CO_3, KCl, $CaCl_2$, and LiBr enhanced the catalytic activity and the aldehyde selectivity [48].

The hydroformylation of myrcene using P-donor ligand-modified rhodium and platinum-tin catalysts was studied and the major products of the reaction identified [49]. 2-Benzyloxy- and 2-tosyloxystyrene were hydroformylated under various reaction conditions with the aim to obtain the corresponding linear aldehydes. The best results (up to 70% linear aldehyde at 80 °C and low pressure) were obtained by using the catalyst precursor $Pt(XANTPHOS)Cl_2$ in toluene or the water-soluble catalytic system $Rh(CO)_2(acac)$/2,7-bis$(SO_3Na)_2$-XANTPHOS in the biphasic medium water/toluene [50].

See also Refs. [9,27].

1.2. *Heterogeneous systems*

1.2.1. *Supported complexes*

Rhodium-complexed dendrimers supported on a resin were evaluated as catalysts for the hydroformylation of aryl olefins and vinyl esters. Up to 99% yields and outstanding selectivity for the branched aldehydes were obtained at room temperature and 69 bar $CO{:}H_2 = 1{:}1$. The dendritic catalysts were recycled by simple filtration and reused even up to the tenth cycle without loss of activity and selectivity [51]. Nafion-supported rhodium–phosphine complexes were investigated for their activity as catalysts in the hydroformylation reaction of 1-hexene. It was found that in comparison to the homogeneous system the overall yield and the ratio of normal heptanal to branched products are reduced by introduction of the catalyst into Nafion [52].

The asymmetric olefin hydroformylation catalyzed by a highly cross-linked polystyrene-supported (*R*,*S*)-

BINAPHOS–Rh(I) complex was investigated in a solvent-free system [53] and in benzene suspension [54]. *Cis*-2-butene and 3,3,3-trifluoropropene were converted into the corresponding iso-aldehydes with high selectivities; 100% regioselectivity and 80% ee for *cis*-2-butene, 93% regioselectivity and 90% ee for 3,3,3-trifluoropropene was observed [53,54].

Heterogenization of $HRh(CO)(PPh_3)_3$ tethered through phophotungstic acid to zeolite Y support [55] or anchored in zeolite Na–Y and MCM-41 and MCM-48 mesoporous materials [56] was found to give novel hydroformylation catalysts with excellent stability, reusability and even improved activity. The activity, selectivity and stability of these catalysts for hydroformylation of a variety of linear and branched olefins was demonstrated [55,56]. A $HRh(CO)(PPh_3)_3$-derived SiO_2-tethered catalyst via thiol ligands was found to be not only effective and stable for cyclohexene hydroformylation at 100 °C and 28 bar $CO:H_2 = 1:1$, but also more active than the corresponding homogeneous catalyst [57]. Aminated MCM-41-tethered $Rh_4(CO)_{12}$ catalyst was found to show good activity, selectivity and recycling in the hydroformylation reaction of cyclohexene [58].

Neutral or cationic rhodium complexes, $[Rh(COD)(\mu\text{-}S(CH_2)_{10}CO_2H)]_2$ and $[Rh(COD)(\eta^6\text{-benzoic acid})]BF_4$ were used as polymer-supported catalysts in hydroformylation of 4-vinylanisole and the effect of the size of the immobilizing supporters on the catalytic activity was investigated at 55 °C and 46 bar $CO:H_2 = 1:3$. It was found that the cobalt-ferrite nanomagnet-supported cationic rhodium catalyst show a high catalytic activity comparable with that of the homogeneous cationic rhodium catalyst, and can be easily recovered from the reaction mixture by magnetic decantation [59,60].

The effect of process parameters of 1-hexene hydroformylation using heterogeneous rhodium catalyst in supercritical carbon dioxide was investigated. The rate constants of heptanal formation at different temperatures were determined, which give an activation volume of $-474\,cm^3\,mol^{-1}$ and an activation energy of $31.9\,kJ\,mol^{-1}$ for the hydroformylation reaction [61]. The effect of solvents in hydroformylation of 1-hexene on the activity of rhodium supported on active carbon catalyst was studied at 30 °C and 30 bar $CO:H_2 = 1:1$. Excellent activity in *n*-octane solvent, but poor activity in water or in alcoholic solvents was found [62].

Non-porous fumed-silica nanoparticles were used as supports to immobilize the water-soluble complex $HRh(CO)(TPPTS)_3$ to obtain supported aqueous-phase catalysts for hydroformylation of 1-hexene. It was found that in comparison with conventional porous granular silica support the aqueous-phase catalyst on non-porous fumed silica support show a better performance in hydroformylation [63].

Rhodium complexes have been entrapped inside the porous systems of inorganic or hybrid matrices via the sol–gel method, and the resulting materials were tested as catalysts in hydroformylation reactions of 1-hexene and 1-decene [64]. Catalysts obtained by heterogenization of $Rh(acac)(CO)_2$, $Rh(acac)(CO)(PPh_3)$, and $RhCl(CO)(PPh_3)_2$ on zinc aluminate spinel were used in hydroformylation of 1-hexene at 83 °C and 10 bar $CO:H_2 = 1:1$ [65]. Supported ionic liquid-phase catalysts by immobilizing rhodium–monophosphine complexes [66] and rhodium–bisphosphine complexes [67] in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate on a silica support were found to be active catalysts in continuous gas- and liquid-phase hydroformylation of propene and 1-octene [66,67].

The hydroformylation of 1-hexene and 1-octene at 100 °C and 0.9 bar CO pressure in 80% aqueous 2-ethoxy-ethanol using poly(4-vinylpyridine)-immobilized rhodium amine complexes as the catalyst was studied. Based on the observed turnover frequencies for the aldehyde production the reactivity order: $2\text{-picoline} > 4-\text{picoline} > 2,6-\text{lutidine}$ was established for the amine component in the catalyst [68,69].

Hydroformylation of 1-hexene was performed at 100 °C in supercritical carbon dioxide (pressure = 186 bar) using silica and mesoporous MCM-41 supported platinum catalysts with $SnCl_2{\cdot}2H_2O$ (Sn:Pt = 3.5:1) as co-catalyst. No hydrogenation was observed and high regioselectivity to heptanal was obtained [70].

The gas-phase hydroformylation reaction of propene using supported aqueous-phase rhodium-NORBOS modified catalysts in a continuous flow reactor was studied. The catalytic performance of silica gel-based catalysts was examined by altering catalyst composition and reaction conditions. Results were compared to analogous TPPTS catalysts and to catalysts supported on alternative support materials [71].

The kinetics of the $[Rh_2(m(S^tBu)_2(CO)_2(TPPTS)_2]$-catalyzed hydroformylation of 1-octene [72] and linalool [73] by supported aqueous phase catalysis was investigated. The effect of temperature, substrate and catalyst concentration and partial pressure of H_2 and CO on the rate of reaction was studied. The activation energy was found to be 17 [72] and 14.5 kcal/mol [73], respectively.

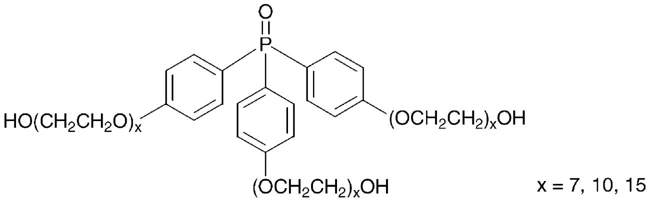
See also Ref. [11].

1.2.2. Biphasic systems

The hydroformylation of 7-tetradecene with a cobalt-TPPTS catalyst was studied in microemulsions as reaction media at various temperatures, pressures and surfactant concentrations. The influence of metal concentration and ligand excess on activity and selectivity was investigated. Yields of more than 50% terminal aldehyde were obtained. A change in the selectivity for linear aldehyde at different temperatures and metal to ligand ratios was attributed to a shift in the equilibrium between modified and unmodified cobalt species [74].

The hydroformylation of 1-dodecene catalyzed by $RhCl(CO)(TPPTS)_2$-BISBIS in aqueous/organic two-phase system was studied. High activity (TOF = 740 h^{-1}) and excellent regioselectivity (96.5% of tridecanal) were obtained at 120 °C and 20 bar pressure with [BISBIS]/[Rh] ratio of 3 in the presence of CTAB [75]. The rhodium-catalyzed hydroformylation of 1-dodecene was investigated with a series of sulfonated water-soluble phosphine ligands such as $Ph_2P(CH_2)_2S(CH_2)_2SO_3Na$ and $Ph_2P(CH_2)_2S(CH_2)_3SO_3Na$ at 120 °C and 60 bar CO:H_2 = 1:1. The ratio of 1-dodecene/rhodium could be increased up to 10.000. Turnover numbers >50.000 and about 65.000 were achieved without any surfactant or in the presence of polyoxyethylene–polyoxypropylene–polyoxyethylene triblock co-polymer, respectively [76].

A novel water-soluble phosphine oxide **24** proved to be an efficient ligand for rhodium-catalyzed hydroformylation of 1-decene at 100 °C and 70 bar CO:H_2 = 1:1, leading up to 93% yield of aldehyde with a *n*:*iso* ratio of 32:68 [77]. The same catalyst was found to be efficient for the hydroformylation of oleyl alcohol as well [78].



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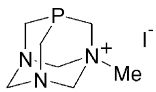
The in situ catalyst from $RhCl_3 \cdot 3H_2O$ and *N*,*N*-dipolyoxyethylene-substituted-2-diphenylphosphino)phenylamine was used in the aqueous-organic biphasic hydroformylation of 1-decene. At 120 °C and 50 bar CO:H_2 = 1:1 up to 99% yield of aldehydes was achieved, which remained as high as 94% after the catalyst has been recycled 20 times [79]. New water-soluble phosphine complexes of rhodium(III) and ruthenium(II) with the ligand 25 were tested as catalysts for two-phase hydroformylation of 1-hexene. At 60 °C and 35 bar CO:H_2 = 1:1 pressure 93% yield of heptanals (59% *normal* and 34% *iso*) was achieved [80].



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Hydroformylation of 1-dodecene catalyzed by the water-soluble rhodium–phosphine complex $RCl(CO)(TPPTS)_2$ in the presence of various mixed micelles was investigated. Mixed micelles were formed from solutions of cetyl pyridium bromide by addition of dodecylbenzenesulphonate, sodium dodecyl sulfate, Triton X-100, or Brij 35. Higher conversion and higher regioselectivity was found in the mixed micellar solution than in the single micelle of cetyl pyridium bromide [81]. In hydroformylation of 1-octene with rhodium/TPPTS catalyst the emulsion formation was found to be minimized and the initial reaction activity showed a maximum at a CTAB/TPPTS ratio of 3 [82].

The influence of pH on the rate of hydroformylation of *p*-methoxystyrene and *p*-fluorostyrene was studied in aqueous solutions using $[Rh(\mu\text{–}OMe)(COD)]_2$ and tetrasulfonated-1,3-bis(diphenylphosphino)propane or (*S*,*S*)-2,4-bis(diphenylphosphino)pentane as the catalyst precursors. At neutral pH, the asymmetric hydroformylation of *p*-substituted styrenes was found to provide low conversion but enantioselectivities as high as 66% [83].

Hydroformylation of 1-butene catalyzed by water-soluble rhodium–TPPTS and rhodium–BISBIS complexes in aqueous two-phase catalytic system was studied. The effects of reaction parameters on the catalytic activity and regioselectivity were investigated. Under the optimum reaction conditions at 130 °C, 25 bar CO:H_2 = 1:1, and [BISBIS]/[Rh] = 5, [1-butene]/[Rh] = 10,400, the turnover frequency and the regioselectivity for *n*-valeraldehyde were found to be 2987 h^{-1} and 98%, respectively [84].

The micellar effect in hydroformylation of 1-octene and 1-decene using water-soluble rhodium complexes with sulfonated diphosphines in the presence of ionic surfactants and methanol in water was studied. The hydroformylation activities using cetyltrimethylammonium hydrogensulfate and methanol additives were found to be higher than those in experiments without these additives [85]. The effect of cetyltrimethylammonium bromide on the performance of the biphasic catalytic system $RhCl(CO)(TPPTS)_2$/TPPTS in long-chain olefin hydroformylation was studied [86].

The biphasic rhodium-catalyzed hydroformylation of 1-octene with the amphiphilic phosphines: $4\text{-}(R)C_6H_4(OCH_2CH_2)_nP(Ph)CH_2CH_2SO_3Na$ (R = 2,2,4,4-tetramethylbutyl, n = 1.4, 5.1, 11.2; R = *n*-nonyl, n = 1.6, 5.6, 11.4), and $RP(Ph)CH_2CH_2SO_3Na$ (R = *n*-octyl, $CH_3(OCH_2CH_2)_2OCH_2CH_2$) was studied. It was found that ligands with a hydrophobic group and a short polyether chain lead to the higher conversion [87]. The catalytic performances of rhodium complexes with new amphiphilic phosphine ligands bis-(3-sodium sulfonatophenyl)-(4-*tert*-butylphenyl)phosphine, phenyl-(3-sodium sulfonatophenyl)-(4-*tert*-butylphenyl)phosphine, and bis-(4-*tert*-butylphenyl)-(3-sodium sulfonatophenyl)phosphine in hydroformylation of 1-hexene, 1-octene, and 1-dodecene was studied. It was found that the rhodium complexes with the new phosphines show significant enhancements in the reaction rate and higher selectivities toward the normal aldehydes in comparison with those obtained by TPPTS and TPPDS rhodium complexes under identical conditions [88].

The rhodium-sulfoXANTPHOS-catalyzed hydroformylation of 1-octene in ionic liquids was studied by high pressure infrared and NMR spectroscopy. It was found that in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate an increase in H_2 partial pressure has no effect on the activity of the system, and similar bis-equatorial and equatorial-apical (diphosphine)Rh$(CO)_2$H catalytic species are present as observed in organic solvents [89].

See also Refs. [11,50,71–73,95].

1.3. Coordination chemistry related to hydroformylation

Structures and energies of cobalt carbonyls, $[Co(CO)_n]^m$ (m = 0, 1+, 1−) and $HCo(CO)_n$, were computed at the B3LYP density functional level of theory [90]. The potential energy surface of the full catalytic cycle of propene hydroformylation with $HCo(CO)_3$ as an active catalyst was investigated at the B3LYP/6-311+G(d)* level. All species involved in the catalytic cycle were fully characterized to be energy minimum structures for the intermediates or saddle point structures for the transition states. It was found that the regioselectivity is determined by the stability of the alkyl cobalt tetracarbonyl complexes, and the rate-determining step is hydrogen coordination rather than oxidative addition [91].

Time-resolved spectroscopic techniques following flash photolysis of acylcobalt carbonyl complexes of the type $RC(=O)Co(CO)_3(PR_3')$ (R = Me, CD_3, Et; R′ = Ph, ^{n}Bu) were used to study transient species that are models for reactive intermediates in cobalt-catalyzed hydroformylation [92].

A variable-temperature multinuclear NMR study using enriched ^{13}CO has shown that the $HRh(CO)_2(TPP)_2$ (TPP = 1,2,5-triphenyl-1H-phosphole) complex, the resting state of the catalytic system for the hydroformylation of styrene by the Rh/TPP mixture, exists in solution as two stereoisomers in equilibrium. The minor isomer (10%) exhibits a geometry where the hydride ligand occupies an equatorial position [93].

Quantum mechanical calculations at the MP4(SDQ)//MP2 level of theory were carried out to investigate the energies and reaction mechanism for the propene insertion reaction into the Rh-H bond, using the $HRh(CO)_3$ as the catalytic species [94].

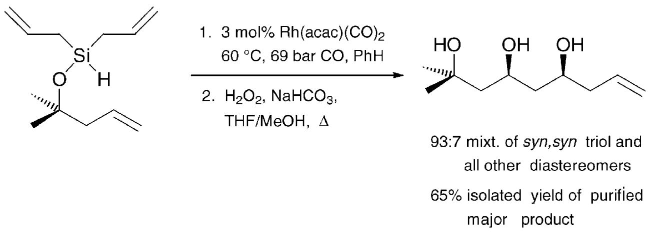
1.4. Engineering aspects of hydroformylation

A new reactor design for catalytic fluid–fluid multiphase hydroformylation reaction was developed by which olefins up to 1-octene were converted to aldehydes at reasonable space-time yields and with high selectivity [95]. The continuous rhodium-catalyzed hydroformylation of low volatility alkenes such as 1-dodecene in supercritical fluid–ionic liquid biphasic systems was investigated. It was found that under certain process conditions, the supercritical fluid–ionic liquid system can be operated continuously for several weeks without any visible sign of catalyst degradation [96].

2. Hydroformylation related reactions of CO

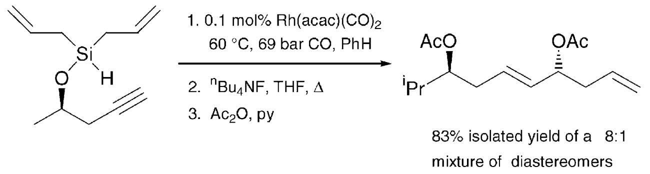
2.1. Silylformylation and silylcarbocyclization

Tandem intramolecular silylformylation-allyl(crotyl)silylation reactios were developed both for alkene and alkyne substrates having a diallylsilane substituent to obtain 1,3,5-triols or 1,5-diols, respectively in a very efficient manner [97]. For example:



93:7 mixt. of *syn,syn* triol and all other diastereomers

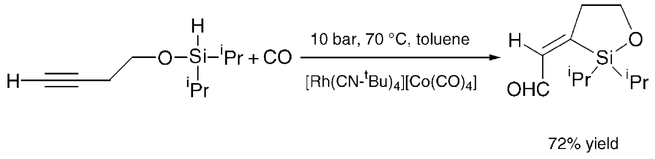
65% isolated yield of purified major product



83% isolated yield of a 8:1 mixture of diastereomers

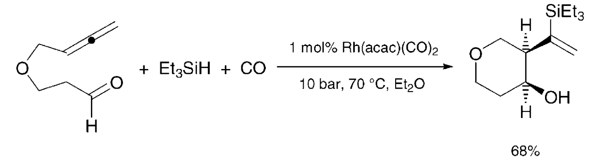
This tandem silylformylation-crotylsilylation reaction was used as the key step to establish the C(23)–C(27) 1,5-*syn*-diol in the synthesis of the C(15)–C(30) fragment of dolabelides [98].

Geometrically defined α,β-unsaturated aldehydes were prepared by a rhodium catalyzed intramolecular silylformylation of homopropargyl silyl ether under carbon monoxide atmosphere [99]. For example:

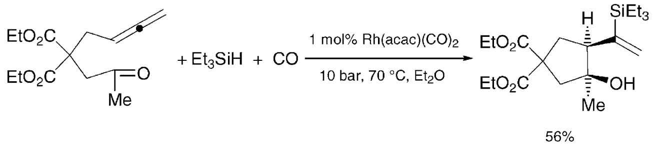


72% yield

A procedure for the synthesis of *cis*-2-triethylsilylvinyl-cyclopentanols and -cyclohexanols from allenyl-aldehydes and -ketones with Et_3SiH through rhodium-catalyzed silylative carbocyclization was described [100]. For example:



68%



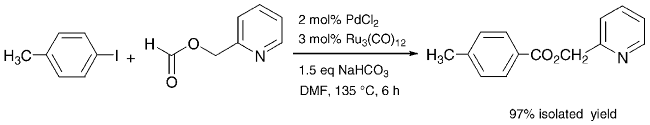
56%

2.2. Hydroxycarbonylation, hydroalkoxycarbonylation and alkoxycarbonylation

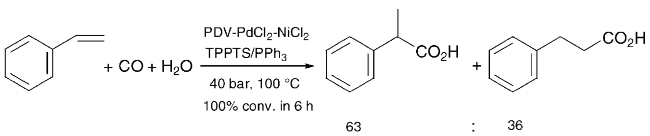
The mechanism of the pyridine-modified cobalt-catalyzed hydromethoxycarbonylation of 1,3-butadiene was studied by high-pressure IR and NMR spectroscopy. It was found that pyridine accelerates the conversion of η^3-$C_4H_7Co(CO)_3$ to methyl-3-pentenoate and the methanolysis of the intermediate $CH_3CH{=}CHCH_2C({=}O)Co(CO)_4$ [101].

A rhodium-based catalytic system, $[RhCl(CO)_2]_2$/MeI/HCOOH/AcOH/PPh_3, was found to allow hydroxycarbonylation of cyclohexene or hexenes to proceed in up tu 96% yield without the need of CO gas at 160–190 °C [102].

An efficient cooperative catalyst system for the coupling of a wide range of organic electrophiles with chelated formate was reported to afford aryl and alkenyl esters by the simultaneous employment of ruthenium and palladium catalyst, in which ruthenium first promotes chelation-accelerated decarbonylation of formate to release carbon monoxide and carbinol that are presumed to be transferred, still chelated to ruthenium, into the palladium catalyst, which catalyzes alkoxycarbonylation of the organic electrophiles [103]. For example:



The polymer-supported bimetallic catalyst system PVD-$PdCl_2$-$NiCl_2$/TPPTS/PPh_3 (PVD = polyvinylpyrrolidone) was found to have good activity in the hydroxycarbonylation of styrene under aqueous-organic two-phase condition and can be reused four times with little loss of catalytic activity. The effects of temperature, CO pressure, and reaction time were studied to obtain optimum reaction conditions [104].

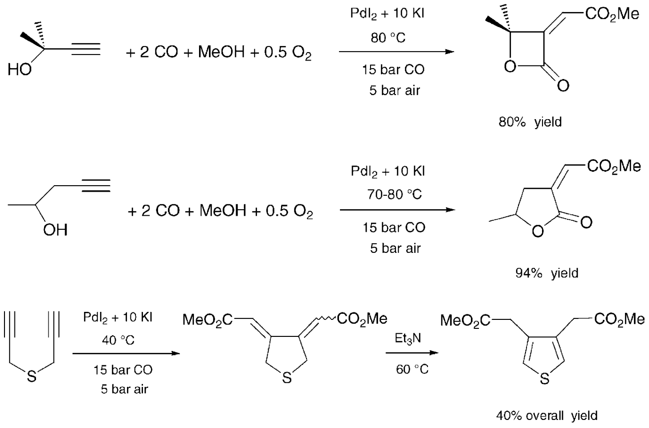


A new method suitable for screening and small scale product synthesis was developed for palladium-catalyzed parallel carbonylation of aryl halides with CO and various alcohols under pressure [105]. The palladium-catalyzed reaction of aryl and vinyl halides or triflates in the presence of acetic anhydride and lithium formate as a condensed source of carbon monoxide was found to provide an efficient simple route to the synthesis of the corresponding carboxylic acid [106].

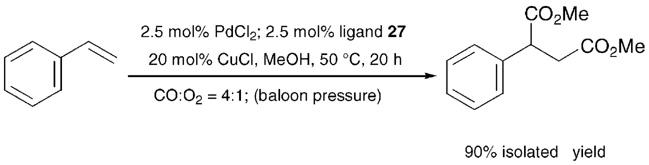
The hydroesterification of acenaphthylene with carbon monoxide and methanol, catalyzed by Pd(II)/PR_3 systems (PR_3 = PPh_3, $P(o\text{-}MeC_6H_4)_3$, $P(p\text{-}MeC_6H_4)_3$, $P(p\text{-}FC_6H_4)_3$, $P(^iBu)_3$, PEt_3, P^cHx_3, $P(OEt)Ph_2$, $P(OPh)_3$, $P(O\text{-}o\text{-}MeC_6H_4)_3$, $P(O{-}^tBuPh)_3$, dppm, dppe, dppp, dppb, dppf, *rac*-BINAP) was found to yield a mixture of acenaphthene-1-carboxylic acid methyl ester, 1-methoxyacenaphthene, and polyacenaphthylene. Using Pd/monophosphine/*p*-TsOH catalyst precursors conversions up to 85% with a chemoselectivity in acenaphthene-1-carboxylic acid methyl ester of 93% were achieved [107]. It was established that the palladium-catalyzed hydroesterification of acenaphthylene takes place through a "hydride" mechanism, that is, through the selective *cis* insertion of the olefin into the palladium-hydride bond [108].

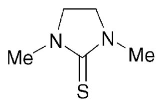
A silica-supported chitosan–palladium complex was found to give good conversion (96.1%) and high regioselectivity (95.3%) to form methyl 3-(6′-methoxy-2′-naphthyl)propanoate in carbonylation of 6-methoxy-2-vinylnaphthalene [109].

A simple catalytic system, consisting of palladium(II) iodide in conjunction with an excess of potassium iodide, was found to be suitable for the direct one-step synthesis of a variety of heterocyclic ester-derivatives in an oxidative cyclization-alkoxycarbonylation reaction from alkynes [110]. For example:



Thiourea-based ligands were evaluated for the palladium-catalyzed bis(methoxycarbonylation) of terminal olefins. The best results were obtained by using tetrasubstituted thioureas such as **26** and **27** [111]. For example:





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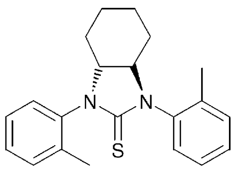
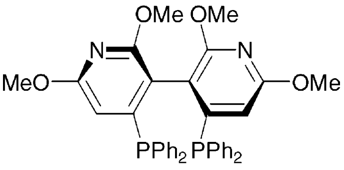


27

Chiral dipyridylphosphine ligands such as **28** were found to be effective in the palladium-catalyzed asymmetric bis-methoxycarbonylation of styrene, reaching up to 84% ee and

79% chemoselectivity for dimethyl-2-phenylsuccinate under the optimal conditions (50 °C, 152 bar CO, styrene/1,4-benzoquinone = 0.5, styrene/Pd = 62.5) [112].

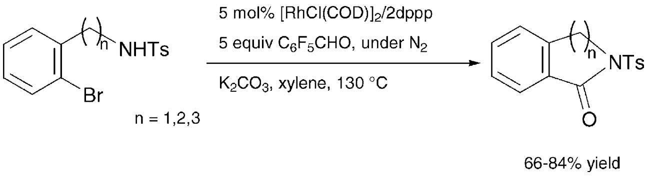


28

The mechanisms of carbonylation of alkenes, alkynes, and alcohols, including the mechanism of oxidative carbonylation of alkynes in the regime of self-oscillations catalyzed by Pd(II), Pd(I), or Pd(0) complexes were analyzed. It was shown that the main reasons for the appearance of self-oscillations in the oxidation reactions are nonlinear and autocatalytic steps of generation and termination of active centers [113].

2.3. Aminocarbonylation, amidocarbonylation, and hydroaminomethylation

The reaction of *N*-Ts-(2-bromophenyl)alkylamines with aldehydes as a source of carbon monoxide in the presence of a catalytic amount of a rhodium complex was found to give five-, six-, and seven-membered benzolactams by an intramolecular aminocarbonylation of the aryl halides [114].



The use of $[\mathrm{bmim}]^+[\mathrm{BF}_4]^-$, $[\mathrm{bmim}]^+[\mathrm{BF}_6]^-$, and $[\mathrm{emim}]^+[\mathrm{BF}_6]^-$ ionic liquids as solvents in homogeneous palladium-catalyzed aminocarbonylation of 17-iodo-5α-androst-16-ene at 100 °C and atmospheric carbon monoxide pressure was investigated. It was found that after the extraction of the product with toluene, the ionic liquid–catalyst mixture can be recycled several times. The activities of the in situ palladium(0) catalysts prepared from $Pd(OAc)_2$ and phosphine ligands, PPh_3, TPPTS, and dppba were compared [115]. γ-Lactams were synthesized from *N*-tosylhomoallylamines by an oxidative carbonylation reaction catalyzed by palladium and copper salts under the normal pressure of CO and O_2 at room temperature. Monocarbonylation was found by the use of $[PdCl_2(MeCN)_2]$ and $CuCl_2$ to afford 3-methyl-2-pyrrolidones, while the use of $PdCl_2$ and CuCl switched the reaction from monocarbonylation to dicarbonylation to produce alkyl 2-oxopyrrolidine-3-acetate in good yields, respectively [116].

The influence of various reaction conditions in the synthesis of *N*-acetyl-α-aminobutyric acid by amidocarbonylation of propionaldehyde with acetamide in the presence of palladium catalysts was studied [117]. The platinum-catalyzed amidocarbonylation of aldehydes with amides and carbon monoxide was described. In contrast to preced palladium catalysis, a remarkable ligand acceleration by phosphine was observed [118].

Hydroaminomethylation of terminal as well as internal aliphatic and aromatic olefins with various amines in the presence of [Rh(COD)(Imes)Cl] as a catalyst was described. Good to excellent yields and high chemoselectivities were obtained In THF at 85–105 °C using 0.1 mol % of catalyst [119]. Highly selective phosphine modified rhodium-catalyzed enamine synthesis from olefins was described [120]. In the presence of various phosphine ligands, especially that of XANTPHOS, cationic rhodium catalysts were found to be useful for highly selective hydroaminomethylation of olefins [121].

See also Refs. [18,28,31].

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

New dipyrido[3,2-a:2′,3′-c]phenazine ruthenium complexes were found to show high catalytic activity in the water–gas shift reaction in a basic medium at 100 °C and $P(\mathrm{CO}) = 0.9\,\mathrm{bar}$ [122]. Iridium complexes, *cis*-$[Ir(CO)_2(py)_2][PF_6]$ and $Ir_4(CO)_{12}$ in 80% aqueous pyridine were found to be active catalysts at 100 °C and 1.9 bar CO for the homogeneous water–gas shift reaction [123].

Various nitroaromatics were reduced to the corresponding anilines under water–gas shift conditions by using solutions of rhodium(III) chloride in aqueouos amines as the catalysts. Tetramethylenediamine and 2-picoline were found to give the most active catalytic systems [124].

2.5. Reduction of CO_2

The electrochemical reduction of carbon dioxide catalyzed by a cofacial dinuclear cobalt(I) porphyrin was investigated [125]. The electrocatalytic carbon dioxide reduction to carbon monoxide and formic acid was studied in aqueous media on glassy carbon electrode coated with polymeric cobalt-tetra-3-aminophenylporphyrin. The redox couple responsible for the catalysis was found to be Co(II)/Co(I) [126]. The simultaneous reduction of carbon dioxide and nitrate ions was investigated at gas-diffusion electrodes with various metallophthalocyanine (M-Pc, M: Ti, V, Cr, Mo, Fe, Ru, Co, Ni, Pd, Cu, Zn, Cd, Ga, In, Ge, Sn, and Pb) catalysts [127].

3. Reviews

(1) Bite angle effects in diphosphine metal catalysts: steric or electronic? A review on the effects of wide bite an-

gles of bidentate phosphine ligands among others in rhodium catalyzed hydroformylation with 103 references [128].

(2) Synthetic aspects of stereoselective hydroformylation. A review with 48 references on new and efficient concepts making use of substrate-direction to control stereoselectivity throughout the course of the hydroformylation reaction [129].

(3) Rhodium diphosphine hydroformylation. A review of density functional and quantum mechanical/molecular mechanical calculations in hydroformylation [130].

(4) Homogeneous catalysis: new approaches to catalyst separation, recovery, and recycling. A review with 40 references of difficulties associated with separating the product from the catalyst [131].

(5) Innovative solvent for two-phase catalysis: ionic fluids. A review with 40 references [132].

(6) The better solution? Chemical synthesis in supercritical carbon dioxide. A review with 30 references of the fascinating applications in heterogeneous, organometallic and enzymatic catalysis in supercritical carbon dioxide [133].

(7) Hydroformylation of alkenes: an industrial view of the status and importance. A review with 392 references [134].

(8) Alcoholysis of acylpalladium(II) complexes relevant to the alternating copolymerization of ethene and carbon monoxide and the alkoxycarbonylation of alkenes. A review with 207 references [135]

(9) Chiral aminophosphine phosphinite ligands and related auxiliaries: recent advances in their design, coordination chemistry, and use in enantioselective catalysis. A review with 76 references [136].

(10) Concepts in homogeneous catalysis: the industrial view. A review with 146 references [137].

(11) Design of carbon–carbon bond forming reactions starting from the oxidative addition of a hydrosilane to a Rh(I) complex. A review with 61 references of recent results on rhodium-catalyzed carbon–carbon bond forming reactions [138].

Acknowledgements

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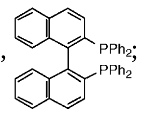
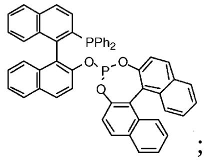
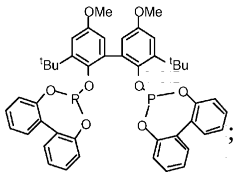
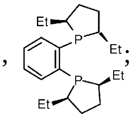
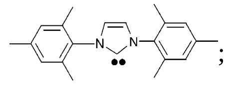
Appendix A. List of abbreviations

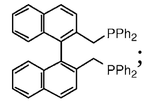
Ac, acetyl; acac, acetylacetonate; Ar, aryl; BINAP, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, 

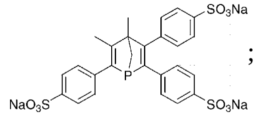
; BINAPHOS, 

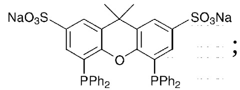
; BIPHEPHOS, 

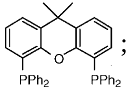
; BISBIS, sodium salt of sulfonated 2,2′-bis(diphenylphosphinomethyl)-1,1′-biphenyl; $[bmim]^+$, 1-butyl-3-methylimidazolium cation; Bn, benzyl; bpy, 2,2′-bipyridine; Bu, butyl; COD, 1,5-cyclooctadiene; Cp, cyclopentadienyl; CTAB, cetiltrimethylammonium bromide; DMF, *N,N*-dimethylformamide; dppb, $Ph_2PCH_2CH_2CH_2CH_2PPh_2$; dppba, 4-(diphenylphosphino)benzoic acid; dppe, $Ph_2PCH_2CH_2PPh_2$; dppf, 1,1-bisdiphenylphosphino)ferrocene; dppm, $Ph_2PCH_2PPh_2$; dppp, $Ph_2PCH_2CH_2CH_2PPh_2$; ee, enantiomeric excess; $[emim]^+$, 1-ethyl-3-methylimidazolium cation; Et, ethyl; Et-DuPHOS, 

; FTIR, Fourier transform infrared; ^{c}Hx, cyclohexyl; Imes, 1,3-dimesitylimidazol-2-ylidene, 

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

; NBD, norbornadiene; NORBOS, 

; Ph, phenyl; py, pyridine; sc, supercritical; SulfoXANTPHOS, 

; THF, tetrahydrofuran; Tf, triflate (trifluoroacetyl); TMS, trimethylsilyl; TOF, turnover frequency (mol product/mol cat/time); 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, 

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Appendix B. The metals and their associated references

Metal	References
Ti	[46,127]
Zr	[45]
V	[127]
Cr	[127]
Mo	[127]
W	[9]
Mn	[47]
Fe	[127]
Ru	[42–44,80,103,122,127]
Co	[1,74,90–92,99,101,125–127]
Rh	[2–41,44–47,50–73,75–89,93–100,102,114, 119–121,124,128,130,131,138]
Ir	[28,123]
Ni	[27,104,127]
Pd	[103–113,115–117,127,135]
Pt	[49,50,118]
Cu	[111,116,127]
Zn	[27,65,127]
Cd	[127]
Ga	[127]
In	[127]
Ge	[127]
Sn	[49,70,127]
Pb	[127]

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