TRANSITION METALS IN ORGANIC SYNTHESIS: HYDROFORMYLATION, REDUCTION AND OXIDATION

ANNUAL SURVEY COVERING THE YEAR 1984*

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I. Theoretical Calculations

Results of CO hydrogenation on supported Rh catalysts were correlated with results of EHMO calculations of the electronic structure of $Rh_4(CO)_{12}$ [1].

The breaking of the H-H bond in H_2 and a C-H bond in CH_4 on both discrete transition metal complexes and on Ni and Ti surfaces was studied by orbital analysis and the extended Hückel method [2]. Reaction mechanisms of the oxidative addition of H_2 to $Pt(CH_3)_2$ and the reductive elimination of CH_4 from $Pt(H)(CH_3)(PH_3)_2$ were studied by ab initio RHF and CI calculations [3]. The mechanism of the cationic Rh-phosphine complex-catalyzed hydrogenation of alkenes has been studied by EHT MO calculations. The results support a dihydride-type intermediate [4]. MO calculations of $H_2Rh(C_2H_4)ClL_2$

(L = substituted Ph_3P), a species directly involved in homogeneous catalytic hydrogenation by Wilkinson's complexes, indicate that the substituents have little effect on the kinetics of the hydrogenation. EHMO calculations of $H_2Rh(C_2H_4)X(PH_3)_2$ (X = Cl,Br) show in agreement with experimental observations that substitution of Cl^- by Br^- favors hydrogenation [5].

A theoretical model was provided that describes the metal-peroxide bonding in peroxo-metal complexes and explains why the metal-bound "peroxy anion" can readily transfer oxygen to nucleophilic alkenes [6].

See also [223].

II. Hydroformylation and Related Reactions of CO

1. Hydrogenation of CO to Hydrocarbons and Oxygen-containing Organic Compounds

The reduction of CO to methane by sodium amalgam is catalyzed by Cp_2VCl_2 + PhOH. The actual catalyst is vanadocene on the amalgam surface [7]. The liquid-phase hydrogenation of CO at 260°C with $Co(acac)_2$ + $LiAlH_4$ as catalyst in THF-tetralin produced hydrocarbons with 85% selectivity to olefins [8].

Homogeneous hydrogenation of CO is catalyzed by $Ir_4(CO)_{12}$ in a variety of solvents at 250°C and 2000 bar (H_2:CO = 1:1) producing preferentially MeOH and methyl formate. In n-pentane as solvent amines were found to be effective promoters while phosphines had a beneficial effect on the selectivity to methanol. Halide promoters gave rise to increased selectivities of C_2-products [9]. Synthesis gas (H_2:CO = 1-2:1) is converted to esters at 100-230°C and 250-400 bar using homogeneous Ru + Rh catalysts (ratio 1-10:2) containing halide promoters in AcOH as solvent [10]. The production of C_1-C_3 alcohols and esters from synthesis gas with a $Ru_3(CO)_{12}$ + $Co_2(CO)_8$ catalyst in molten Bu_4PBr has been investigated in detail. Highest yields of ethanol were achieved at Ru/Co ratios between 1 and 2. Most of the Ru and Co present in the reaction mixture could be accounted for on the basis of the species $Co(CO)_4^-$, $HRu_3(CO)_{11}^-$ and $Ru(CO)_3Br_3$. There was no direct spectroscopic evidence for the formation of mixed-metal carbonyls. The C_1-C_3 alcohols did not follow the Schultz-Flory distribution which is in accordance with other evidence, that the C_1 and C_2 fractions are coming from different catalytically active intermediates [11,12].

2. Hydroformylation

a) Co Catalysts

High pressure IR and UV measurements confirm the Heck mechanism of the hydroformylation of 1-octene and cyclohexene with $Co_2(CO)_8$ as the starting catalyst. The reaction between the acylcobalt carbonyl $RCOCo(CO)_4$ and H_2 has been found to be the major pathway at 80°C and 95 bar ($CO:H_2 = 1:1$) whereas the alternative reaction between $RCOCo(CO)_4$ and $HCo(CO)_4$ is only a minor pathway. The activation of the catalyst precursor $Co_2(CO)_8$ is the slowest step of the reaction [13]. The relative distribution of all C_9 aldehydes resulting from the hydroformylation of the 42 octene isomers using $HCo(CO)_4$ has been determined. Me groups in the branched olefins inhibited hydroformylation at the tertiary carbon and at the carbon near to it, promoting reaction at the terminal carbon atoms. Aldehyde product distributions did not vary greatly with conversion [14]. A mathematical model for propene hydroformylation with a cobalt-phosphorous catalyst in a packed bubble reactor was described [15].

Cracking, hydrogenation, aldol condensation, and formate formation accompanied hydroformylation of dicyclopentadiene in the presence of catalyst systems comprising $Co_2(CO)_8$ and PR_3 (R = Ph, Bu, Me, or cyclohexyl) or pentaphenylphosphole. The yields of dicyclopentadienedimethanol did not exceed those obtained with $Co_2(CO)_8$ alone as catalyst [16]. Hydroformylation of ethene or propene with CO + H_2 and $Co_2(CO)_8$ + ditertiary phosphine catalysts gave mainly ketones (C_5 and C_7) at the expense of aldehydes [17]. Hydroformylation of olefins was performed with $HCo(CO)_4$ or $HCo(CO)_3PBu_3$ as catalysts simultaneously synthesized electrochemically from a cobalt anode in the autoclave. The amount of catalyst necessary for the same conversion and the induction period were smaller than without electrolysis [18].

The kinetics of isobutene hydroformylation with $RCCo_3(CO)_9$ clusters as catalysts has been studied. The activity of the clusters decreased in the order R = Pr > H > Ph > EtOOC > Cl [19].

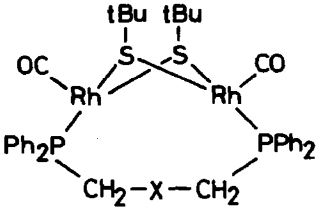
See also [20,38,39].

b) Rh Catalysts

Hydroformylation of some olefins has been investigated under mild conditions (25-50°C, 1 bar) using as catalyst precursors $Co_{4-n}Rh_n(CO)_{12}$ + L systems or preformed $Rh_4(CO)_{12-x}L_x$ clusters (L = tertiary phosphine or phosphite; n = 0, 2, or 4; x = 1-4). Among the mixed-metal clusters, n = 2 showed the highest activity but this effect disappeared with time and the complex disproportionated into homometallic clusters. According to IR spectroscopy if L = phosphite, all Rh was in the form of $Rh_4(CO)_9L_3$ but if L = phosphine, fragmentation to dinuclear complexes could be observed [20]. 1-Pentene was hydroformylated under the same conditions also with $Rh_4(CO)_{12}$ + x PPh_2H + y L catalyst systems. The combined addition of PPh_2H and the trisubstituted phosphorous ligand resulted in a synergistic effect for x = 1-2 and y = 2-4. Increase of x to 3 or 4 caused a sharp drop in catalytic activity [21].

Hydroformylation of 1-hexene in the presence of $Rh(AA)(CO)(PPh_3)$ or $Rh(AA)[P(OPh)_3]_2$ type complexes (AA = β -diketone or 8-hydroxyquinoline) has been examined. An excess of phosphine or phosphite increased rate and selectivity of the reaction [22]. A comparative study of Ph_3N, Ph_3P, Ph_3As, Ph_3Sb and Ph_3Bi as ligands in the Rh-catalyzed hydroformylation of dodecene-1 at 90°C and 8 bar of H_2/CO showed that regiospecifity, as measured by the n/i product ratio, varies inversely to increased ligand basicity. The maximal conversion to aldehyde (87-95%) was obtained with Ph_3P, while Ph_3Bi inhibited hydroformylation and Ph_3N gave very small conversions [23]. Hydroformylation of 1-heptene at 60°C and 5 bar CO + H_2 using $Rh_2(COD)_2Cl_2$ and $Ph_2P(CH_2)_nPPh_2$ (n = 1-4) as catalyst showed that the selectivity for linear aldehyde formation increases with the phosphine/Rh ratio [24]. The role of α , ω -bis diphenylphosphino alkanes which promote the hydroformylation of substituted terminal olefins with a Rh + PPh_3 catalyst has been discussed [25].

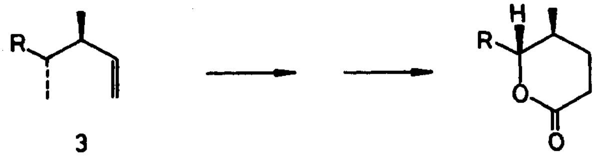
The influence of 32 amines, amino acids, N-heterocycles and urea derivatives on the hydroformylation of propene catalyzed by $Rh(CO)(PPh_3)_2Cl$ has been investigated. N-containing compounds with very low basicity increased aldehyde selectivity and the n/i ratio [26]. In the hydroformylation of allyl- (estragole, safrole, eugenol), as well as propenylbenzenes (anethole, isosafrole, isoeugenol) to the corresponding aldehydes at 5 bar pressure and 80°C the catalyst precursor $Rh_2(\mu\text{-}SCMe_3)_2(CO)_2[P(OMe)_3]_2$ proved to be more selective than $HRh(CO)[PPh_3]_3$. The latter caused extensive isomerization of allylbenzenes [27]. The heterobimetallic complex (1) catalyzes the hydroformylation of 1-hexene at 80°C and 5 bar $CO+H_2$. The analogous complex (2) is somewhat less active which is attributed to the Zr center inducing more electron density on the Rh atoms [28].



1, X = $Cp_2Zr<$

2, X = $-CH_2CH_2-$

Glycols are produced by hydroformylating vinyl acetate or allyl acetate with Rh complexes as catalysts at 70-150°C to $AcOCH_2CH_2CHO$ and AcOCHMeCHO or $AcOCH_2CHMeCHO$ and AcOCHEtCHO, respectively, which may be converted to the corresponding alkanediols [29]. Several homoallylic alcohols (3) were hydroformylated with a $Rh+PPh_3$ catalyst and the resulting aldehydes oxidized with pyridinium chlorochromate to give δ-lactones (4) in excellent yields [30].



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(E)-N-propenylphthalimidine (5) and N-allylphthalimidine were hydroformylated with $HRh(CO)(PPh_3)_3$ + (-)-DIOP (7) [or (-)-DIOCOL (8)] catalysts. With (5) as substrate complete regioselectivity to (6) was achieved but the allyl compound yielded both possible aldehydes in roughly equal amounts. Practically no optical induction was observed [31].

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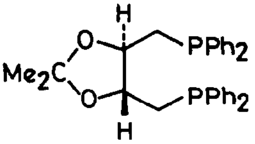
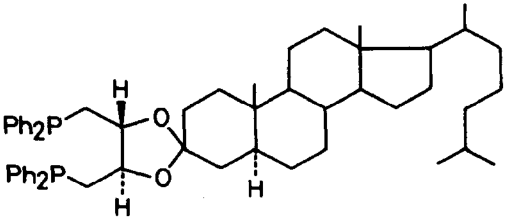
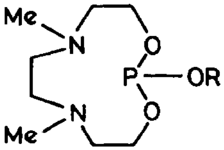


7, (-)-DIOP



8, (-)-DIOCOL

The potentially tridentate ligands (9) were prepared and used in the form of RhCl(CO)(L) complexes (L = 9) as catalysts for the hydroformylation of olefins. The catalysts were active even at 40°C, but those ligands which contained a chiral R group were ineffective in providing asymmetric induction in the hydroformylation of styrene [32].



9, R = Me, Et, sec-Bu, (S)-(-)-2-methyl-1-butyl, menthyl

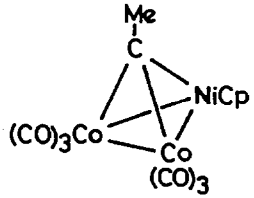
The homogeneous catalyst $[(NBD)RhCl(amphos)]NO_3$, [amphos $= Ph_2P(CH_2)_2N^+Me_3$], prepared from amphos nitrate and $[(NBD)RhCl]_2$ showed catalytic activity for alkene hydrogenation and hydroformylation in a two-phase system [33]. The homogeneously dissolved Rh catalyst was regenerated from hydroformylation reaction products containing PhMe as solvent by extracting with water-soluble phosphines like $P(C_6H_4SO_3Na)_3$, Ph_2PCH_2COONa or $PhP(CH_2COONa)_2$ [34]. An apparatus for the hydroformylation of ethene to EtCHO and recycling the $HRh(CO)(PPh_3)_3$ catalyst was described [35].

See also [199].

c) Other Metals

Hydroformylating propene in toluene solvent with $Cp_2Fe_2(CO)_4$ as catalyst at 100-150°C and 70-140 bar CO + H_2 the complex $HFe(CO)_2Cp$ has been detected by infrared spectroscopy in samples taken from the reaction mixture. About 35% of the dimer is converted under such conditions to the hydride which probably plays a similar role in the catalytic cycle as $HCo(CO)_4$ in the Co-catalyzed system [36].

Heptyne-1 and -2 and heptene-1 were partially hydrofomylated and hydrogenated at 140°C and 50 bar (H_2:CO = 1:1) using $Ir(L)(COD)(PPh_3)$ or $[Ir(L)(COD)]_2$ as catalysts (L = pyrazolate) in the presence of PPh_3 [37]. The rate of hydroformylation of cyclohexene was greatly increased on using $Co_2(CO)_8$ + $Ru_3(CO)_{12}$ mixed catalysts compared with $Co_2(CO)_8$ or $Ru_3(CO)_{12}$ alone. Kinetic studies revealed that the rate of aldehyde formation is first order in Co and 0.6 order in Ru. A similar synergistic effect was also observed if the mixed metal cluster $FeCo_3(CO)_{12}^-$ was used as catalyst, but $Co_2(CO)_8$ + $Fe_3(CO)_{12}$ mixed catalysts were not better than Co alone [38]. The mixed metal clusters (10)-(15) have been tested as catalysts for the hydroformylation of pentene-1 (at 130°C) and styrene (at 70°C). Cluster (15) decomposed to $Co_2(CO)_8$ under the reaction conditions but the other five clusters remained apparently intact and could be recovered with high yield. Rather long reaction times were used (1-6d) suggesting either a very low catalytic activity of the clusters or the formation of very small amounts of active fragments [39].



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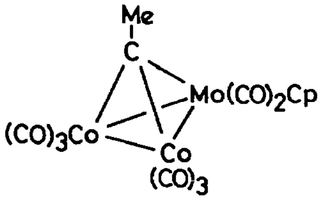

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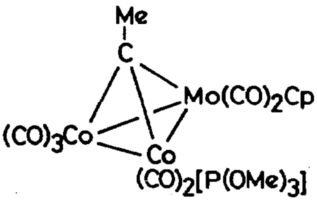

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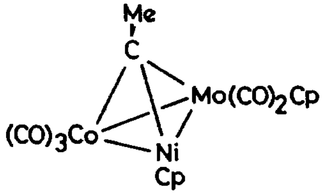

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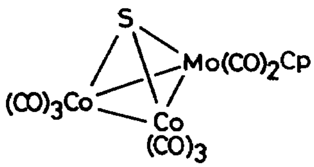

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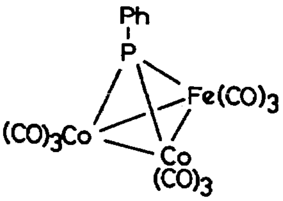

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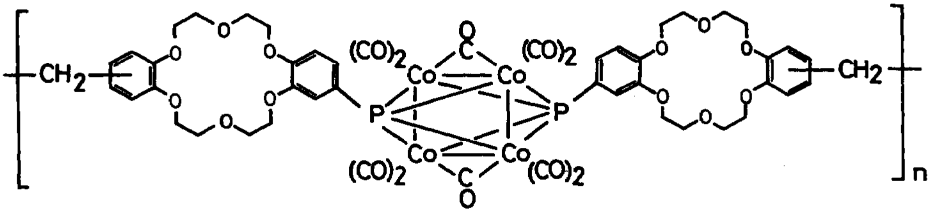
See also [163].

d) Heterogeneous Systems (Supported Complexes)

Complexes of $Co_2(CO)_8$ with phosphinated silica gel have been prepared and tested as catalysts for the hydroformylation of propene at 100-170°C under CO pressures of 0.3-10 bar. Rate constants were determined [40]. The supported metal cluster catalyst $[Co_4(CO)_{10}](\mu_4\text{-}PR)_2]$ (R = polystyrene - divinylbenzene copolymer) having a Co content of 9.5% catalyzed the hydroformylation of 1-hexene to heptanals with 83% conversion and 100% selectivity [41]. The same tetranuclear phenylphosphide Co carbonyl cluster supported on polymer crown ether (16) was found to be more active for hydroformylation of terminal olefins then when the cluster alone was used as a homogeneous catalyst [42].



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Molecular sieve-enclosed rhodium carbonyl catalysts were prepared and used for the hydroformylation of aliphatic olefins at 130°C and 85 bar synthesis gas [43]. Simultaneous vapor-phase hydrogenation and hydroformylation of propene over Rh-exchanged X and Y zeolites in a reactant stream consisting of propene:H_2:N_2:CO (3:3:2:1) at atmospheric pressure resulted in butyraldehyde/isobutyraldehyde ratios of 2.0/1 and 1.9/1, respectively. After hydroformylation IR spectroscopy showed the presence of $Rh_6(CO)_{16}$ on zeolite Y [44]. Ethene and propene were hydroformylated over a Rh-Y-zeolite catalyst. It was concluded, that the active sites at the surface can catalyze the hydroformylation of both substrates but that the active sites formed in the pores even at a very short distance from the entrance can catalyze only the hydroformylation of ethene [45].

The rate of EtCHO formation in ethene hydroformylation over a Rh-Y zeolite at atmospheric pressure was found to be approximately proportional to ethene partial pressure and proportional to the square root of H_2 partial pressure; the rate of aldehyde formation decreased as the CO partial pressure increased. Almost no isotope effect on the reaction rate was observed using D_2 instead of H_2 [46].

Gas-phase hydroformylation of ethene has been performed over Pd-exchanged silica catalysts at 70°C and atmospheric pressure. Best results were obtained with silica gel supports, strongly acidic supports like silica-alumina were found unsuitable. Only minor amounts of ethane were formed [47].

e) Modified Hydroformylations

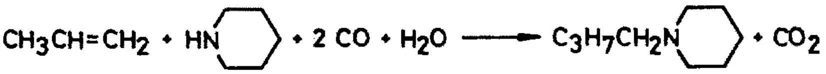
The $Co_2(CO)_8$ + dppe catalyst system catalyzes the hydroformylation of olefins with CO + H_2O resulting in aldehydes:

$$RCH{=}CH_2 + 2CO + H_2O \longrightarrow RCH_2CH_2CHO + CO_2$$

the hydrocarbonylation of olefins with CO + H_2O resulting in ketones:

$$2RCH{=}CH_2 + 2CO + H_2O \longrightarrow (RC_2H_4)_2CO + CO_2$$

the hydroformylation of olefins with CO + H_2 and the aminomethylation of propylene with CO + H_2O:



Highest catalytic activities were found around P:Co = 1:1. Ketone formation is the main reaction at high olefin:Co ratios [48]. Propene yields butanols, butyric acids and dipropyl ketones as byproducts [49]. Other ditertiary phosphines give catalysts with lower catalytic activity [50].

C_5 or C_7 dialkyl ketones were formed from ethene or propene, CO and H_2 in aqueous CF_3COOH solutions at 30-70°C with Pd(II) - PPh_3 complexes as catalysts. Reaction rate was highest in the presence of about 5% water in the solvent [51].

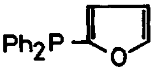
3. Homologation of Alcohols, Carboxylic Acids and Esters with $CO + H_2$

Homologation of methanol to acetaldehyde

$$CH_3OH + CO + H_2 \longrightarrow CH_3CHO$$

can be performed with $Co(OAc)_2.4H_2O + I_2$ as catalyst at 140°C and 300 bar. Cyclic ethers and glymes have a beneficial effect on the selectivity of the reaction. In tetraglyme, for example, MeOH is converted to acetaldehyde with nearly 100% conversion and 86% selectivity [52]. The kinetics of the reaction has been studied using a $Co(OAc)_2 + PPh_3 + MeI$ catalyst. A first order dependence for methanol, cobalt acetate and CO was found. For H_2 an order of 0.4, for MeI an order of 2 and for PPh_3 an order of -2 was established. The oxidative addition of MeI to a Co species is regarded as the rate determining step [53]. Addition of $PtCl_2$ to a $Co(OAc)_2.4H_2O + LiI$ catalyst increased the reaction rate. The role of the platinum is to accelerate the reduction of Co^{2+} to $Co(CO)_4^-$ [54].

The homologation of methanol to ethanol has been investigated using the "supported liquid phase catalyst" method with $RuCl_2(CO)_2(PPh_3)_2 + CoI_2 + NaI + PPh_3$ as catalyst system at 180-200°C and 100-200 bar. Carbowax 1500 was used as solvent and Chromosorb as support. Unusually high selectivities of ethanol (and propanol) formation were obtained and no ethers were observed as byproducts [55]. Synthesis of ethanol in tetraglyme or a cyclic ether as solvent with $Co(OAc)_2.4H_2O$, $Ru(acac)_3$ and I_2 as catalyst was performed in two stages. First at 140°C acetaldehyde was produced and then hydrogenated by increasing the temperature to 200°C. In this way over 85% yield was obtained [56]. The novel, potentially bi- or tridentate phosphines (17), (18) [57] and (19) [58] were used as ligands with a $Co(OAc)_2.4H_2O + RuCl_3.3H_2O + I_2$ (or MeI) catalyst system at 155-200°C and 300 bar $CO + H_2$. Best MeOH conversion was 70% and EtOH selectivity 40%.



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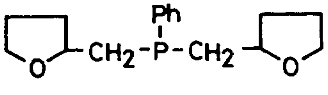

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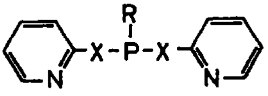

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R=Me, tBu, Ph

$X=CH_2$, O, NH

Propionic acid reacts with synthesis gas ($CO:H_2$ = 1:1) in the presence of a $RuO_2.xH_2O$ + quaternary phosphonium salt catalyst to form alkyl propionate esters. Reaction conditions are 220°C and 430 bar. The primary product is methyl propionate but at sufficiently long reaction times the ethyl ester becomes predominant [59].

Formic and higher molecular weight carboxylic acid esters react with CO/H_2 at 200°C and 150-200 bar pressure in the presence of ruthenium carbonyl iodide systems as catalysts. Hydrogenation, carbonylation and homologation on both the alkyl and the acyl moiety of the molecules take place. A mixture of derivatives of higher homologous acids and alcohols is formed [60]. The effect of some coreagents and ligands in the Ru-catalyzed homologation of methyl acetate to ethyl acetate has been tested. Water decreases the selectivity to C_2 products whereas N-bases, such as pyridine or piperidine have a beneficial effect [61].

4. Coordination Chemistry Related to CO Hydrogenation and Hydroformylation

The examination of model systems [i.e. $HMn(CO)_5$ or $HRu_3(CO)_{11}$] for the homogeneous catalytic reduction of CO show that intra- and intermolecular hydride transfer paths are involved in the conversion of metal hydrides to formyls [62].

The chemistry of cobalt carbonyls in the presence of butadiene under hydroformylation conditions has been studied by IR spectroscopy. At 80°C and 95 bar CO + H_2 cobalt is mainly present in the form of η^3-$C_4H_7Co(CO)_3$. In methanol solution the formation of this complex is incomplete and the remaining H^+ and $Co(CO)_4^-$ catalyze hydroformylation [63]. The formation of $HCo(CO)_4$ from $Co_2(CO)_8$ and H_2 was studied under high pressure with IR and UV spectroscopy. Kinetic data lead to the conclusion that under the conditions typical for syn-gas reactions catalyzed by $HCo(CO)_4$ the hydride is predominantly formed via an associative pathway which is not inhibited by CO [64].

The reaction

$$CH_3(CH_2)_4COCo(CO)_4 + HCo(CO)_4 \longrightarrow CH_3(CH_2)_4CHO + Co_2(CO)_8$$

proceeds by second order kinetics and is not retarded by CO. A mechanism was proposed which involves the fast reversible homolysis of the acyl compound followed by H abstraction from the hydride in the rate-controlling step. The kinetic data suggest that in stoichiometric hydroformylation the initial π-complexation of the olefin with $HCo(CO)_3$ is the slow step [65]. The kinetics and the product distribution of the reaction between $HCo(CO)_4$ and 2,3-dimethyl-1,3-butadiene was investigated. The reaction starts with the concerted 1,4-addition of the hydride to the s-<u>cis</u> conformation of the diolefin. 2,3-Dimethyl butene-1 and -2 are formed as hydrogenation products along with acyl and π-allyl type Co carbonyl complexes [66]. 3,3-Dimethylbutene is stoichiometrically hydroformylated at -15°C with a mixture of $HCo(CO)_4$ and $HCo_3(CO)_9$. Under the same conditions there is no reaction in the presence of $HCo(CO)_4$ alone. Labeling experiments show that in the aldehyde formed the H atom of the formyl group has come from $HCo(CO)_4$ and the other H atom from $HCo_3(CO)_9$ [67]:

$$DCo(CO)_4 + HCo_3(CO)_9 + Me_3CCH{=}CH_2 \longrightarrow Co_4(CO)_{12} + Me_3CCH_2CH_2CDO$$

The cocondensation of Co atoms with ethene at 77 K generates a labile cobalt-ethene complex $(C_2H_4)_mCo_n$. Addition of CO and H_2 to this complex results in the hydroformylation of ethene and reduction of CO [68].

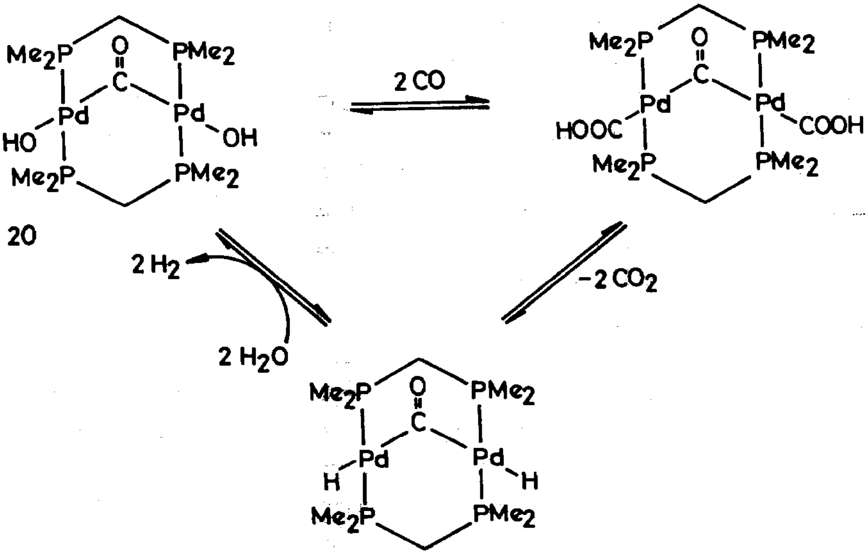
$HRh(CO)(PPh_2R)_3$ complexes are highly stable and act as reversible reservoirs for the generation of reactive carbonyl hydride intermediates for 1-alkene hydroformylation to n-aldehydes. Catalyst stability and activity videly varies if R is branched at the α or β position [69]. The IR spectrum of $HRh(CO)(PPh_3)_3$ bound to phosphinated gel-form polystyrene-divinylbenzene beads was recorded at ambient temperature and 18 bar CO + H_2 pressure, at different CO and H_2 partial pressures. Two predominant species were observed at $CO{:}H_2 = 0.67{:}1$, a dimer and $HRh(CO)_2(PPh_3)_2$. An increase of H_2 partial pressure increased the concentration of the hydride. In the presence of 1-hexene hydroformylation took place under the conditions employed [70].

The P-C bonds of p-substituted triphenylphosphines were found to be cleaved under hydroformylation conditions (200°C, 300 bar synthesis gas) in the presence of Rh, Co or Ru carbonyls. Main products were ArH, ArCHO and $ArCH_2OH$. Tributylphosphine was stable under these conditions [71]. Triphenylphosphine is converted slowly into propyldiphenylphosphine during low-pressure propene hydroformylation with $HRh(CO)(PPh_3)_3$ catalyst. The reaction starts with the reversible oxidative addition of the phenyl-phosphorus bond to Rh. In the absence of CO (hydrogenation conditions) the formation of propyldiphenylphosphine is much faster [72]. Several group 8 transition metals catalyze intermolecular aryl scrambling of triarylphosphines under an atmosphere of H_2 and propene at 120--170°C. Following an induction period Co was the most active. With Rh mixed aryl-propyl phosphines were also formed [73].

The kinetics of the stoichiometric reaction of MeR_3N^+ cations with $HFe(CO)_4^-$ and $Mn(CO)_5^-$ was investigated in terms of its relationship to the catalytic homologation of methanol to ethanol with CO and H_2 (Annual Survey 1982, ref.53,54). In case of the manganate system, the product selectivity (ethanol vs. methane) was independent of H_2 or CO pressure [74].

5. Water Gas Shift Reaction

Kinetic studies with the water gas shift reaction catalyst precursor, $Ru_3(CO)_{12}$ as well as previous investigations with $Fe(CO)_5$ and $M(CO)_6$ (M = Cr, Mo, W) showed the dissociative path being favored relative to the associative one [75]. The water gas shift reaction catalyzed by $Ir_4(CO)_{12}$ in alkaline 2-ethoxyethanol /water solution is first order in base and in Ir, and zero order in CO. The rate determining step of the catalytic cycle is the reaction between OH^- and $HIr_4(CO)_{11}^-$ [76].



The dinuclear complex $Pd_2Cl_2(dmpm)_2$ dissolved in water is catalytically active at 77°C and 1 bar. The actual catalyst is (20) formed by reversible substitution of Cl^- by OH^- and uptake of CO. The catalytic cycle suggested [77] is shown on the preceeding page.

The ruthenium carbonyl complexes anchored to silica via phosphine ligands, $Ru(CO)_4(PPh_2C_2H_4\text{-SIL})$ and $H_4Ru_4(CO)_8(PPh_2C_2H_4\text{-SIL})$, catalyze the water gas shift reaction at 150°C. The mononuclear complex is about one order of magnitude more active than the tetranuclear one [78]. The anionic triruthenium cluster $HRu_3(CO)_{11}^-$, anchored to silica via ammonium or pyridinium functional groups, exhibits high catalytic activity at 100-150°C. According to IR spectra the triruthenium cluster framework remains intact up till 150°C [79]. Various aminated polystyrenes were examined as supports for $Rh_6(CO)_{16}$ used as catalyst in 2-ethoxyethanol solvent at 80°C. The polymer prepared from chloromethylated polystyrene and diethylenetriamine was found to be the most effective [80]. Transition metal ions in zeolite form high valent carbonyl complexes which are reduced by H_2O + CO or H_2 + CO mixtures to mono- and polynuclear metal carbonyl complexes. These show catalytic activity in CO insertion into organic substrates and in the water gas shift reaction [81].

The iron carboxylic acid anion $Fe(CO)_4COOH^-$ is an important intermediate of the water gas shift reaction catalyzed by $Fe(CO)_5$. Its formation from $Fe(CO)_5$ and OH^- hydrates in the gas phase and its stability towards decarboxylation was studied. It was concluded that the anion must be deprotonated before losing CO_2 [82]. Stoichiometries and conditions for the condensation of $HM(CO)_4^-$ to $HM_3(CO)_{11}^-$ for M = Fe, Ru and Os have been determined. Under water gas shift conditions /100°C and 1 bar CO/ the mononuclear Ru anion rapidly trimerizes but $HFe(CO)_4^-$ does not form $HFe_3(CO)_{11}^-$. The $HOs(CO)_4^-$ anion is more active in the water gas shift reaction than $HOs_3(CO)_{11}^-$ [83].

6. Reduction with CO + H_2O

Polynuclear aromatic and heteroaromatic compounds were selectively reduced under water gas shift conditions, or with synthesis gas or H_2 using Fe, Mn, Co, Rh, Ru, Cr, Mo or W carbonyls as catalysts. Polynuclear heteroatomic N compounds were more reactive and the heterocyclic ring was reduced regioselectively [84]. Iron pentacarbonyl in the presence of H_2O, CO, base and a phase-transfer agent catalyzes the reduction of nitrogen heterocycles regiospecifically in the nitrogen-containing ring at 150-300°C. Anthracene is also reduced in the 9,10 positions by this system; 9,10-dimethylanthracene yields nearly equal amounts of the cis- and trans-dihydro products. Results suggest an electron transfer process as the mechanism of hydrogenation [85].

Nitrobenzene is not reduced by CO + H_2O with $Rh_6(CO)_{16}$ as catalyst precursor. Addition of phen or substituted 1,10-phenanthroline derivatives leads, however, to active catalyst systems. Aniline yields of 100% may be achieved at 165°C 30 bar CO. Mononuclear Rh carbonyls substituted by phen or its derivatives are regarded as active catalysts [86]. Nitroarenes were transformed into the corresponding aminoarenes in high yields at 80°C with CO + H_2O using a catalyst system composed of $Pt(PPh_3)_2Cl_2$ + $SnCl_4$ + + Et_3N. Chloro and methoxy substituents were not affected [87].

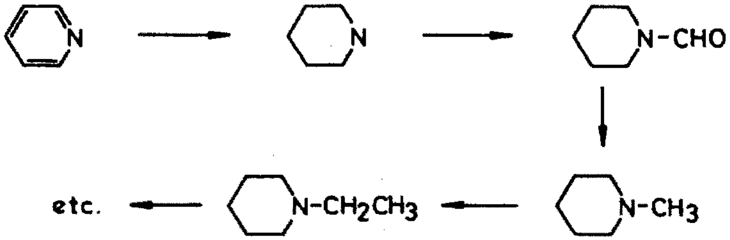
7. Miscellaneous Reductive Transformations of CO and CO_2

Hydroformylation of olefins with a $Co_2(CO)_8$ + PR_3 catalyst at high pressures (70-280 bar, H_2:CO = 2:1) yields significant amounts of formates which are formed in a secondary reaction from aldehydes, CO and H_2:

$$RCHO + H_2 + CO \longrightarrow RCH_2OOCH$$

Highest yields of formates (46%) were achieved with phosphines having small cone angles, like PEt_3 or PMe_3 [88].

Synthesis gas in the presence of $Co_2(CO)_6(PPh_3)_2$ precatalyst effects the hydrogenation, carbonylation and subsequent homologation of pyridine to N-alkylpiperidines:



Reaction conditions are 212°C and 80 bar. N-methylpiperidine is also homologated under these conditions to the ethyl derivative and labeling experiments show that in this case the reaction starts by the fission of the Me-N bond [89].

Carbon dioxide is reduced to formaldehyde, formic acid and oxalic acid with reducing agents such as Cr^{2+}, V^{2+} or Mo^{5+} in the presence $TiCl_3$-treated zeolite CaA [90]. Carbon dioxide is reduced to alkyl formates in alcohol solutions by H_2 in the presence of the $HM(CO)_5^-$ (M = Cr, W) anionic carbonyl hydrides under rather mild conditions (125°C, 30 bar $CO_2 + H_2$):

$$CO_2 + H_2 + ROH \longrightarrow HCOOR + H_2O$$

Although the water gas shift reaction also takes place under these conditions, experiments with ^{13}CO-labeled catalysts provide evidence against the formation of formates from CO and ROH [91]. The complex $Rh(dppe)_2Cl$ catalyzes the electroreduction of CO_2 in acetonitrile solution. The reduction product is the formate anion, and acetonitrile is the source of the H atom in the product formate [92].

III. Hydrogenation and Reduction

1. H-D Exchange

The H-D exchange between deuterobenzene and $H_7Re(PCy_3)_2$ in the temperature range 60-80°C proceeds over $H_5Re(PCy_3)_2$ formed by reductive elimination of H_2. Deuterium is incorporated into the complex not only as hydride ligands but also selectively at the C2 and C3 carbons of all cyclohexyl rings [93]. The complex $H_4Ru(PPr^i_3)_3$ catalyzes the H-D exchange between deuterated aromatic solvents and PPr^i_3. The reaction is slow with PCy_3, and toluene is less reactive than benzene [94]. The complex $Rh[P(OPh)_3]_2(acac)$ (A) undergoes H-D exchange with D_2 at the ortho positions of the phosphite ligand and at the central methine position of the acac ligand. The data support complete dissociation of Hacac which generates a high degree of coordinative unsaturation at the Rh center. It is suggested that a complex of this type may be involved in the hydrogenation of arenes catalyzed by (A)[95]. Complexes of the type $Pd(PR_3)_n$ (n = 3,4) catalyze the H-D exchange reactions between D_2O and various organic substrates, at ambient temperature. The following order of decreasing rates has been found: $RNO_2 \gg RCN > R_2CO \gg RCOOR, RX, ROR$. For nitroalkanes deuteration occurs only at the C1 position [96]. Copper(I)-coordination to terminal alkynes increases the rate of H-D exchange on the terminal carbon atom with CD_3COOD:

$$RC\equiv CH + CD_3COOD \rightleftharpoons R\equiv CD + CD_3COOH$$

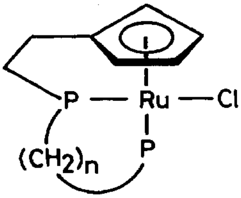
With 1,7-octadiyne the rate increases by a factor of 1.2×10^5. The exchange does not involve alkynide formation [97].

2. Hydrogenation of Olefins

a) Fe and Ru Catalysts

Photocatalytic hydrogenation of ethene with $Fe(CO)_4(C_2H_4)$ as catalyst was investigated in the gas phase. The active species is $Fe(CO)_3(C_2H_4)$. Turnover rate of the process was found to be 900 s^{-1} which is a thousand times larger than that known for the fastest liquid-phase hydrogenation system [98]. The catalyst generated by the laser is thermally active, not photochemically [99]. Unsaturated hydrocarbons could be hydrogenated with $Fe(acac)_3$ as catalyst in the presence of $AlCl_3$.With 1-hexene reaction rate was highest at Al/Fe = 3, and increased with H_2 pressure (10-100 bar) [100]. Activity of $Fe(acac)_3$ + $SnCl_2$ and $Fe(acac)_3$ + $AlCl_3$ catalysts in 1-hexene or 1,3-pentadiene hydrogenation depended on the Al:Fe or Sn:Fe ratio and the method of preparation of the catalysts as well as on the H_2 pressure. The reaction mechanism involves complexation of the alkene to the Fe atom [101]. The iron complex prepared from $Fe(acac)_3$ and dppe in toluene, followed by a treatment with $NaBH_4$ in EtOH, is an active catalyst for the hydrogenation of olefins and dienes [102].

Homogeneous hydrogenation of α-olefins and cycloolefins is catalyzed by Ru(η^6-arene)(η^4-COD) complexes under mild conditions (room temperature, 1-20 bar). The arene ligand probably remains attached to the Ru atom during the catalytic cycle [103]. The kinetics of the homogeneous hydrogenation of cyclohexene using $Ru(PPh_3)_3Cl_2$ as catalyst has been studied. The rate passes through a maximum with increasing catalyst concentration which is probably due to the formation of dimeric species. Low concentrations of Et_3N increase the activity of the system but at higher concentrations the rate decreases [104]. The Ru complexes (21) catalyze the hydrogenation of cyclohexene and of the C-C bond of norbornenone with 100% selectivity and high turnover numbers. Analogous Ru complexes which do not contain a cyclopentadienyl ligand were found to be less selective [105].



21

n = 3,4

The reaction of $RuCl_3.3H_2O$ and a carboxylate polymer (synthesized from a chloromethylated resin) in acetic acid/ethanol and treatment of the supported complex with sodium acetate results is the formation of a polymer-supported ruthenium complex containing bridging acetate groups and showing only minimal Ru elution at 85°C in DMF. Its structure is probably analogous to that of $[Ru_3O(OAc)_6(H_2O)_3]^+$. The activity of this supported complex as olefin hydrogenation catalyst has been studied [106].

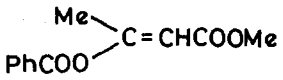
See also [588].

b) Co, Rh and Ir Catalysts

The effect of varying concentrations of $Co(dmg)_2$ catalyst, NaOH, mono-, di-, and trialkylamines on the kinetics of the homogeneous hydrogenation of fumaric and maleic acids was studied. Dialkylamines yielded the most active catalysts [107]. The activity of CoI_2 + $MgBu_2$, $Co(acac)_2$ + $MgBu_2$, $Co(acac)_3$ + MgBuBr, $Co(acac)_3$ + MgBuI, and $Co(acac)_3$ + $MgBu_2$ catalysts in the hydrogenation of various hydrocarbons individually depends on the Co/Mg ratio. Using CoI_2 + $MgBu_2$ in THF at 25° and normal pressure the rate of hydrogenation is norbornene $\gg$ cyclohexene > anthracene $\gg$ naphtalene and the reaction is first order in cyclohexene [108]. The complexes $MeCo(CO)_2[(MeO)_2PC_2H_4P(OMe)_2]$, $MeCo(CO)_3P(OMe)_3$ and $PhCH_2Co(CO)_3PPh_3$ have been used as catalysts for the hydrogenation of 1-alkenes. Each was active but their lifetime was much shorter than that of $MeCo(CO)_2[P(OMe)_3]_2$ [109].

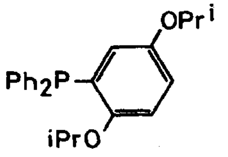
Hydrogenation of atropic acid and its esters with $K_3[HCo(CN)_5]$ in a water solution containing 5% 1,2-dichloroethane is accelerated by the neutral surfactant polyoxyethylene 23 dodecyl ether. This effect is attributable to concentration of the substrate and the catalyst in the micelles [110]. A nonionic surfactant Brij 35 was also useful to promote the $[Co(CN)_5]^{3-}$-catalyzed hydrogenation of styrene in micellar solution. However, the use of dodecyldimethyl(α -methylbenzyl)-ammonium bromide as a phase-transfer agent resulted in more efficient acceleration of the reaction rate [111].

Deuteration of β - acyloxy crotonates (22) catalyzed by $Rh(PPh_3)_3Cl$ is a syn process with very high stereoselectivity. There is no regioselectivity, however, in the addition of HD [112].



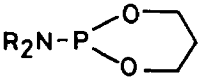
22 (Z and E)

By systematic variation of the phosphine ligand in Rh phosphine complexes the catalytic activity in olefin hydrogenation has been enhanced by a factor of $> 10^4$ relative to the activity of $Rh(PPh_3)_3Cl$. The following modifications were examined: varying the basicity of the ligands, replacing Cl^- by the non-coordinating BF_4^-, use of a chelating diphosphine, and varying the chain length of the diphosphine [113]. The influence of the number, position and structure of OR-substituents on the phenyl rings of tertiary aryl phosphines upon the rate of hydrogenation of 1-hexene using Rh(I)-phosphine complexes as catalysts was investigated. Initial rates varied within three orders of magnitude, the most active catalyst was obtained with (23) as a ligand. Triarylarsines gave generally lower activity catalysts than the corresponding triarylphosphines [114].



23

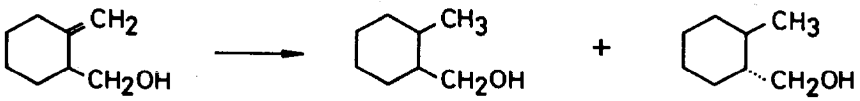
The activity of $Rh(PPh_3)_3X$ (X = Cl, Br, I) complexes as homogeneous catalysts for the hydrogenation of cyclopropene fatty acid Me esters decreased in the order I > Br > Cl. The most active iodo complex was found, however, to be too susceptible to oxidation for practical use [115]. $RhL(CO)_2Cl$ and $RhL(CO)(PPh_3)Cl$ (L = 3-aminocumarin) complexes prepared from $Rh_2(CO)_4Cl_2$ or $Rh(CO)_2(PPh_3)Cl$, respectively, and L, catalyze the hydrogenation of linear and cyclic olefins [116]. The complex $[(L\text{-}L)Rh(NBD)]ClO_4$ reacts with H_2 to yield $[(L\text{-}L)HRh(\mu\text{-}H)_3RhH(L\text{-}L)]ClO_4$, a trihydride-bridged species [(L-L) = rac-Fe(η^5-$C_5H_4PPhBu^t)_2$]. Solutions of this latter complex are catalytic for olefin hydrogenation [117]. Rh(I) complexes of the type Rh(CO)(L)(acac) (L = 24) were used as catalysts for the hydrogenation of 1-heptene at 70°C and 1 bar [118].



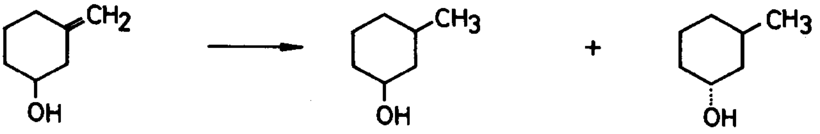
$R_2N = Me_2N, Et_2N, Ph_2N, C_5H_{10}N, OC_4H_8N$

24

Homogeneous hydrogenation of the homoallylic alcohol 2-methylenecyclohexanemethanol (25) with $[Rh(Ph_2PCH_2CH_2CH_2PPh_2)(NBD)]BF_4$ as catalyst afforded the cis and trans alcohols (26a) and (26b) in practically equal amounts. The structurally similar homoallylic alcohol (27), however, could be hydrogenated with over 98% selectivity to the trans alcohol (28b). These results suggest the coordination of the OH group to the Rh atom during hydrogenation [119].

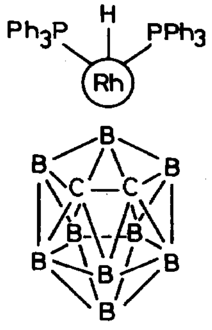


25 26 a 53% 26 b 47%



27 28 a <2% 28 b >98%

Hydrogenation of 3-methyl-3-phenyl-1-butene was studied with several bis (triphenylphosphine)rhodacarborane catalyst precursors. The results prove that the icosahedral cluster does not participate in the catalytic cycle and that the operational catalytic species has a (phosphine)(alkene)Rh(I) exo-nido structure [120]. The two rhodacarborane clusters (29) and (30) were used as catalysts for the hydrogenation of 1-butylacrylate . A catalytic cycle was proposed that involves *exo*-*nido*-rhodacarboranes as intermediates and culminates in the elimination of 1-butylpropionate from such a reversibly formed intermediate (31) [121].



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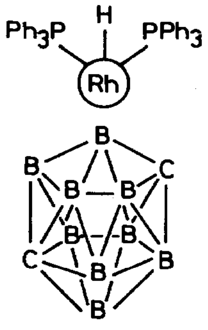

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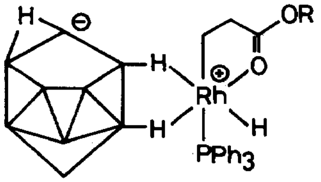
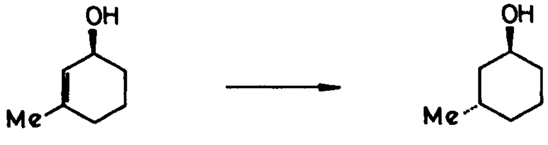


31

Hydrogenation of unsaturated carboxylic acids with Rh(tpm)$_3$Cl as catalyst in water solution has been studied. Excess phosphine had a strong inhibiting effect in the case of crotonic acid whereas with maleic acid no inhibition was observed. These unusually pronounced differences were explained by assuming three parallel catalytic pathways involving cationic Rh complexes, phosphinerhodium chloride complexes and phosphinerhodium carboxylate complexes as catalysts [122]. Biphasic hydrogenation of olefins (e.g. p-MeOC$_6$H$_4$ -CH=CH$_2$), dienes (e.g. 1,4-octadiene), and α , β -unsaturated carbonyl compounds (e.g. PhCH=CHCHO) was carried out using Rh$_2$(HD)$_2$Cl$_2$ as catalyst. α , β -Unsaturated carbonyl compounds underwent selective hydrogenation of the C=C bond. The active catalyst is colloidal Rh [123].

The activity of the catalyst systems formed *in situ* from Rh$_2$(NBD)$_2$Cl$_2$ and (p-RC$_6$H$_4$)$_3$P (R = H, Me, OMe) for the hydrogenation of 1-hexene changes on ageing of the catalyst precursor solution in the presence of air. Two processes are regarded to be responsible for this phenomenon: the oxidation of the phosphine which decreases the P/Rh ratio and a successive degradation which leads to an unidentified catalyst [124].

The cationic Rh(I) complex [Rh(NBD)(dppe)](TsO) proved to be as effective as catalyst for the hydrogenation of soybean oil as the similar complexes containing ClO$_4^-$ or PF$_6^-$ counterions. Binding of the Rh(I) cation to sulfonated polystyrene, however, resulted in a total lack of activity [125]. Polyethylene single crystals were brominated, treated with $LiPPh_2$ and then with $Rh(PPh_3)_3Cl$. The activity of the catalyst obtained in this way was for hydrogenation of cyclohexene significantly higher than that of $Rh(PPh_3)_3Cl$ supported on a polystyrene [126]. The homogeneous catalytic hydrogenation of cyclohexene with the complexes MLCl [M = Rh, Ir; L = $HN(CH_2CH_2PPh_2)_2$] was reported. Kinetic data suggest a mechanism with H_2MLCl species as intermediates [127]. The diastereoselectivity of hydrogenation of cyclic olefinic alcohols like (32) with $[Ir(COD)(PCy_3)py]PF_6$ as catalyst increases with decreasing catalyst concentration. With some acylic olefinic alcohols the complex $[Rh(NBD)(Ph_2PCH_2CH_2CH_2CH_2PPh_2)]BF_4$ exhibits even better diastereoselectivity than the Ir complex [128, 129].



32

See also [33, 134]

c) Ni, Pd and Pt Catalysts

Mixed organometallic catalysts composed of $Ni(st)_2$ + $M(st)_n$ (M = Cr, Fe, Co, Cu) and $AlEt_3$ are more active for the hydrogenation of sunflower oil than the analogous single-metal catalysts obtained from $Ni(st)_2$ and Et_3Al [130].

The effects of temperature, solvent, and additives on the selectivities obtained in the hydrogenation of 3-(2-furyl)acrolein and acrolein were studied using Pd complexes with N-containing ligands as catalysts. Hydrogenation of acrolein was 100% selective for C=C reduction [131]. A polymer Pd complex was prepared from 4,4-diamino-2,2'-bipyridine palladium diacetate and 2,4-toluene diisocyanate. After reduction with $LiAlH_4$ the complex was used as a catalyst for olefin hydrogenation [132]. Palladium acetate anchored to polystyrylbipyridine has been used as catalyst for the hydrogenation of monoalkenes. Terminal olefins were found to hydrogenate more easily than internal ones. Kinetic results indicate that the reaction proceeds via two parallel mechanisms [133]. The olefin isomerization catalyst obtained from $[PtCl_2(SnCl_3)_2]^{2-}$, $[RuCl(SnCl_3)_5]^{4-}$, or $[RhCl_4(SnCl_3)_2]^{3-}$ supported on an anion exchange resin (AV-17-8) are turned into olefin hydrogenation catalysts by addition of K_2ReOCl_5 [134].

See also [202]

d) Other Metals

Photolysis of <u>cis</u>-$HMn(CO)_4PPh_3$ in the presence of H_2 and 1-alkene results in catalytic hydrogenation and isomerization of the alkene. The catalytic cycle can also be entered by use of <u>cis</u>-$MeMn(CO)_4PPh_3$. (Alkyl)$Mn(CO)_4PPh_3$ complexes are intermediates of the reaction [135].

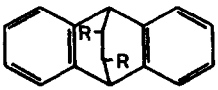
Alumina-silica possessing various Al_2O_3/SiO_2 ratios was reacted with $CpTiCl_3$ and the resulting Ti complexes on the surface reduced by an excess of BuLi. The supported Ti complexes were tested as catalysts for olefin hydrogenation. Active catalysts contained large amounts of Ti(III) and the most active Ti(III) complexes were supported on alumina-silica having ≈50% Al_2O_3 [136].

The polynuclear thorium hydride $[Me_2Si(Me_4C_5)_2ThH_2]_x$ catalyzes the homogeneous hydrogenation of hexenes [137].

3. Asymmetric Hydrogenation of Olefins

Interest in the preparation of new chiral ditertiary phosphines is diminishing. More emphasis was put on the synthesis of chiral aminophosphines or phosphinites and also of phosphines containing additional heteroatoms in the side chain which enhance interactions between the ligands and the substrate.

The enantiomers of the chiral diphosphines (33) and (34) (R = CH_2PPh_2) were prepared and used as ligands in the asymmetric hydrogenation of unsaturated carboxylic acids. Optical yields between 10 and 82% were obtained [138].



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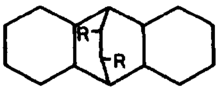
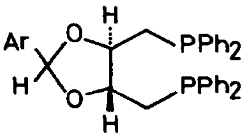
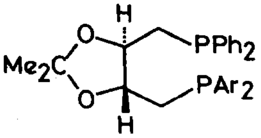


34

The modified DIOPs (35) and (36) were prepared and applied for the asymmetric hydrogenation of α-acetamidocinnamic acid and dehydrodipeptides. Best results were obtained with (36d), the modification at the dioxolane ring (ligands 35) had little effect on enantioselectivity [139].

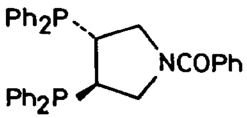


35a, Ar = 2-naphthyl
35b, Ar = 1-pyrenyl



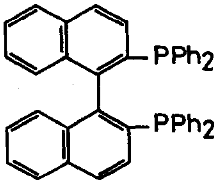
36a, Ar = p-tolyl
36b, Ar = p-methoxyphenyl
36c, Ar = 1-naphthyl
36d, Ar = 2-naphthyl

N,N-bis(diphenylphosphinomethyl)amino acids were used as chiral ligands in the asymmetric hydrogenation of α-acetamidocinnamic acids with $Rh_2(diene)_2Cl_4$ + phosphine in situ catalysts. Optical yields of about 30% were achieved independently of the amino acid used for the preparation of the chiral bisphosphine. These relatively low values were explained by the fact that the 6-membered chelate ring formed by Rh and the ligand in the catalytically active complex may have a nonchiral chair conformation because of the 4-position of the chiral C atom [140]. The chiral ditertiary phosphine (37) has been prepared starting from natural tartaric acid and used as a ligand in the asymmetric hydrogenation of α-acetamidocinnamic acid with Rh complexes. 99% optical yield was achieved even at high pressure (50 bar) and high substrate :catalyst ratio (10000:1) [141].



37

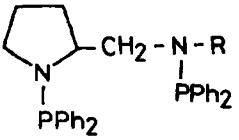
The preparation of both enantiomers of BINAP (38), an atropisomeric bis(triaryl)phosphine has been described in detail. Rh(I) complexes of (R)- and (S)-BINAP catalyze the asymmetric hydrogenation of 2-(acylamino)acrylic acids with 67-100% optical yield [142].



38

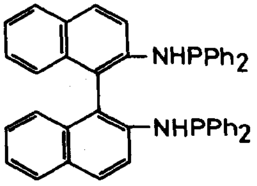
Asymmetric hydrogenation of several oligopeptides containing dehydro phenylalanine was performed using Rh(I) complexes with chiral diphosphines as catalysts. The effect of peptide structure on enantioselectivity was investigated [143]. Asymmetric hydrogenation of (β-heteroaryl-α-acylamido)acrylic acids with Rh(I)-DIOP complexes was investigated. Substrates containing a five-membered ring with one heteroatom were more reactive than those containing a five-membered ring with two heteroatoms or a six-membered heterocycle [144].

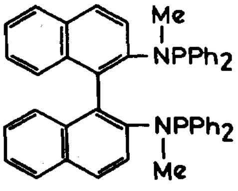
A number of isomerically related chiral bis-aminophosphines (39-41) have been tested as ligands for rhodium catalysts in the asymmetric hydrogenation of α-acetamido-cinnamic and -acrylic acids. Highest enantioselectivities were obtained with ligand (41) [145].



39, R = (S)-(-)-PhMeCH-
40, R = (R)-(+)-PhMeCH-
41, R = $PhCH_2$

The axially dissymmetric diphosphine ligands (42) and (43) were prepared and used in Rh(I)-catalyzed asymmetric hydrogenation of α-acylamidoacrylic acids and esters. Optical yields up to 95% were obtained [146].

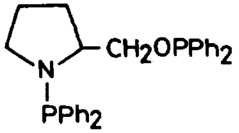




42

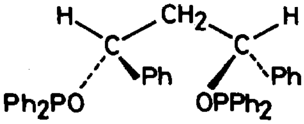
43

Several chiral aminosphosphine-phosphinites were prepared from optically active amino alcohols like ephedrines, prolinol and N-methyl phenylglycinol. The new ligands were tested in asymmetric hydrogenation of α -acetamidoacrylic acid with Rh(I) complexes. The ligand (44) prepared from prolinol afforded optical yields of 70-80%, the others were significantly less enantioselective [147].



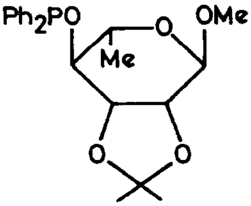
44

Complexes formed in situ from $Rh(COD)_2Cl_2$ and the optically active ligands $S\text{-}PhCH_2CH(NPPh_2Me)CH_2OPPh_2$, (1R,2S)-$PhCH(OPPh_2)CHMeNPPh_2Me$ or (1R,2R)-$PhCH(OPPh_2)CHMeNPPh_2Me$ catalyzed hydrogenation of PhCH=C(NHAc)COOH to give (R)-$PhCH_2CH(NHAc)COOH$ in 2-4% optical yield [148]. The Rh(I) complexes of the new chiral phosphinite (45) act as efficient asymmetric homogeneous catalysts for the hydrogenation of (Z)- α -acylamidocinnamic acids. Optical yields above 90% were achieved [149].



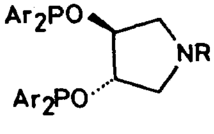
45

The chiral phosphinite (46), a derivative of L-rhamnose was prepared and used as ligand in the asymmetric hydrogenation of prochiral alkenes with Rh(I) catalysts [150].



46

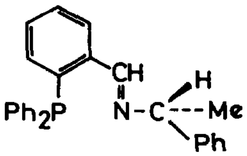
Seven different chiral diphosphinites of the type (47) were used in the form of Rh(I) complexes for the asymmetric hydrogenation of dehydrodipeptides [151], dehydroamino acids and itaconic acid [152]. Extremely high diastereoselectivities (> 98%) due to double asymmetric induction were observed in hydrogenating dehydrodipeptides with ligands containing an ω -dimethylaminoalkyl group.



47

Ar =	R =
Ph	$CH_2CH_2NMe_2$
$p\text{-}MeC_6H_4$	$CH_2CH_2NMe_2$
$p\text{-}MeOC_6H_4$	$CH_2CH_2NMe_2$
Ph	$CH_2CH_2CH_2NMe_2$
Ph	$CH_2CH_2CHMe_2$
$p\text{-}MeOC_6H_4$	$CH_2CH_2CHMe_2$
Ph	CH_2Ph

Asymmetric hydrogenation of (Z)- α- acetamidocinnamic acid was investigated with catalysts formed in situ from $[Rh(COD)Cl]_2$ and the chiral P,N-ligands (49) or (50). The activity of the catalysts was rather low and the optical yields were only 17 and 14%, respectively [153].



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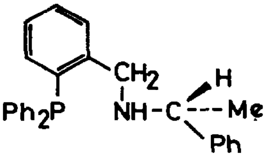
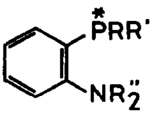


50

18 new optically active phosphines of the types (51) and (52) were tested as ligands for the homogeneous Rh-catalyzed hydrogenation of N-acyl- α-aminocinnamic acids at P:Rh ratios 1.1 and 2.2. Only (53) showed appreciable asymmetric induction (68). A change of configuration of the product formed occurred in some cases by varying the P:Rh ratio [154].



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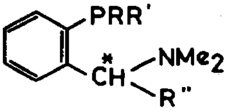

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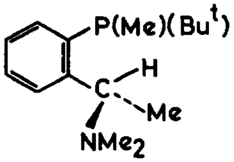
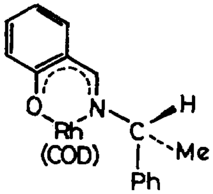
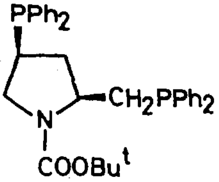


53

Rh complexes containing chelate ligands with asymmetry centers near the N atom, e.g. (54), were used in the hydrogenation of α -acetamidocinnamic acid. The low optical inductions obtained suggest that the catalyst loses its chirality during catalysis due to racemization or fragmentation [155].

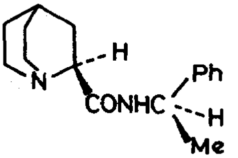

54

Fixed chiral Rh(I) complexes of DIOP or BPPM (55), prepared by treatment of charcoal with metal acetates followed by $Rh_2Cl_2(COD)_2$ and the chiral phosphine, were used as catalysts for the asymmetric hydrogenation of α -acetamidocinnamic acid. The recovered catalyst retained its activity [156].


55

BPPM

The catalyst system $CoCl_2/(+)\text{-nmenPh}_2P/NaBH_4$ afforded in the asymmetric hydrogenation of PhCH=C(NHAc)COOMe to (S)-(+)-$PhCH_2CH$(NHAc)COOMe optical yields of ≤ 60%. The catalyst system (L-isoleucine)$_2$Co/PPh_3/$NaBH_4$ gave a much lower o.y., however [157]. Several chiral tertiary amines with a secondary amide group at the α - or β -carbon (like (56) and (57)] have been prepared and used as cocatalysts in the asymmetric hydrogenation of (58) and (59) with the Co(dmg)$_2$ + achiral base catalyst system. The highest optical yield (79%) was achieved in the hydrogenation of (59) using (56) as chiral ligand [158].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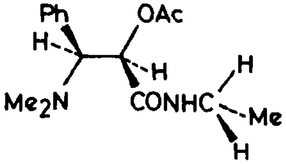
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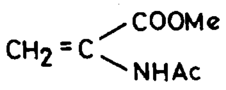

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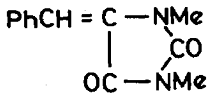


59

Ethyl α -methylcrotonate was hydrogenated with $CoCl_2$[(-)-DIOP] or $NiCl_2$[(-)-DIOP] as catalyst at 80-100°C and 50 bar. Addition of Et_3N increased the conversion, but the activity of the catalysts remained still rather low. Optical yields of 1-12% were achieved [159].

4. Hydrogenation of Dienes and Alkynes

a) Fe, Ru and Os catalysts

During hydrogenation of alkynes and alkenes using the $Fe(st)_3 + AlEt_3$ catalyst system an associated polynuclear complex is formed the amount of which changes parallel with catalytic activity [160]. The catalytic activity of a MoFeS complex supported on poly(vinylpyridine) in the hydrogenation of acetylene is increased by treating the catalyst with a solution obtained by mixing $FeCl_2$ and NaHS in MeCN [161].

$Ru_3(CO)_{12}$, $Ru_2Fe(CO)_{12}$, $RuFe_2(CO)_{12}$ and $Fe_3(CO)_{12}$ all catalyze the hydrogenation of pentynes and pentadienes at 80°C and 1 bar both in toluene solution and anchored to γ -Al_2O_3. Activity of the complexes decreases with increasing number of iron atoms. Anchorage on γ-Al_2O_3 leads to decrease in activity for pentyne hydrogenation but increases activity for pentadiene hydrogenation [162]. Ru(η^4-COD)(η^6-C_8H_{10}) catalyzes the homogeneous hydrogenation of 1,3- and 1,5-COD to cyclooctene at room temperature and 1 atm H_2 in THF or alcohol solvents. 1,5-COD isomerizes to 1,3-COD before hydrogenation [163]. Hydrogenation of Me linoleate using $Ru(PPh_3)_3Cl_2$ as homogeneous catalyst provided cis-monoenes with high selectivity under mild conditions. With $H_2Ru(PPh_3)_4$ or $Rh(PPh_3)_3Cl$ the formation of isolated trans C=C bonds was also minimal, but selectivity for monoene formation was somewhat lower [164].

$H_3CpNiOs_3(CO)_9$ catalyzes the hydrogenation of 1,3-pentadiene in solution at 120°C and 0.9 bar H_2. When supported onto Chromosorb

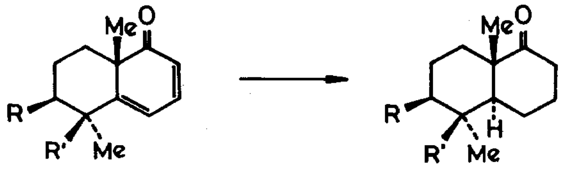
P the activity of the complex depends upon pretreatment. Probably both homogeneous and heterogeneous catalysis occur [165].

See also [171, 264].

b) Co and Rh Catalysts

Several diolefinic terpenes (like limonene, α -terpinene, α -phellandrene, etc.) have been hydrogenated to Δ^1- and Δ^3-menthenes in good yields with $Co_2(CO)_6(PBu_3)_2$ or $HCo(CO)_2(PBu_3)_2$ as catalysts at 70-100°C and 20-30 bar H_2. Attempts to perform asymmetric hydrogenation by using chiral phosphines as ligands failed [166]. Binding of $HCo(CN)_5^{3-}$ to various anion exchange resins provides a stable supported catalyst useful in the three-phase hydrogenation of dienes to monoenes. Water is a necessary ingredient. The catalyst is practically neutral [167]. Acetylenes are regioselectively hydrocyanated by cyanocobaltate prepared at $CN:Co < 5:1$ to give secondary nitriles, and partly hydrogenated to alkenes or saturated hydrocarbons. In the presence of bpy hydrogenation predominates which is attributed to the formation of $Co(CN)_3(bpy)H^-$ [168].

Hydrogenation of the hexahydronaphthalenone derivatives (60) with $Rh(PPh_3)_3Cl$ as catalyst gave the decahydronaphthalenone derivatives (61) in good yield [169].



60 61

60a, 61a: R = H
R' = Me
60b, 61b: R = OH
R' = COOMe

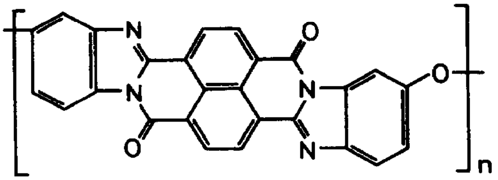
Hydrogenation of 1,5-COD has been studied over catalysts prepared from Merrifield resins loaded with PPh_2 groups and $Rh_2(CO)_2Cl_2$. The yield of cyclooctene did not depend on the P/Rh ratio of the catalysts but the yield of cyclooctane was strongly decreased by increasing the P/Rh parameter. This suggests that the formation of cyclooctane requires the presence of vicinal active sites [170]. Rhodium and ruthenium chloride complexes prepared by mixing the solution of polyethylenimine and the salt in 2:1 and 4:1 N:metal ratios catalyzed the hydrogenation of <u>cis</u>- and <u>trans</u>-$CH_2{=}CHCH{=}CHMe$

mainly to trans- MeCH=CHEt under 5 bar of hydrogen pressure in the presence of $NaBH_4$. Byproducts were 1- and cis-2-pentene and pentane [171].

See also [164, 178, 246].

c) Pd Catalysts

A new, very selective catalyst for the hydrogenation of acetylenes to (Z)-olefins has been prepared from $Pd(OAc)_2$, NaH, and t-pentyl alcohol in THF. The catalyst was self-terminating (did not hydrogenate alkenes to alkanes) [172]. Homogeneous Pd complex catalysts were compared with Pd/C catalysts in the hydrogenation of sorbate, Me linoleate and conjugated linoleate. Selectivity of olefin formation was higher with $Pd(acac)_2$ than with Pd/C. Conjugated linoleate was significantly more reactive than unconjugated linoleate [173]. Pd complexes containing a primary amine ligand and reduced by $(Me_2CHCH_2)_2AlH$ or BuLi are active catalysts for the hydrogenation of acetylenic hydrocarbons to olefins with a selectivity of 98-99% at 95% conversion [174]. O_2 and H_2O activate Pd complex catalysts containing primary amine and sulfide ligands in the selective hydrogenation of conjugated dienes to olefins [175]. The product of the reaction of $PdCl_2$ and trialkylamines deposited on mineral supports (γ-Al_2O_3, zeolite, lanthanide oxides) proved to be a highly active catalyst for selective (> 94%) hydrogenation of dienes to olefins [176]. Palladium chloride on the polymer (62) was active as a catalyst in the hydrogenation of alkynes and CH_2=$CHCH_2OH$ but inactive for benzene, naphthalene, cyclohexanone, octanal, and propargyl alcohol [177].



62

Polyethylenimine complexes $(CH_2CH_2NR)_n.MCl_2$ (R = H, Ac; n = 150-200; M = Pd, Rh, Co, Ni) catalyze the partial hydrogenation of cycloalkadienes and -polyenes to the corresponding cycloalkenes at 20-50°C and 1-5 bar. For example, 1,3- and 1,5-cyclooctadiene and cyclooctatetraene were converted to cyclooctene with 90-94%

selectivity. Catalytic activity decreased in the stated order of M [178].

See also [264].

d) Other Metals

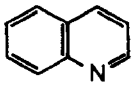
A polymer-supported hydrogenation catalyst, Ⓟ-$CH_2(C_6H_4O)(Cp)_2TiOC_6H_4R$, (Ⓟ = styrene-divinylbenzene copolymer, R = H, Me, tBu) containing ≈6% Ti was prepared and used for the hydrogenation of cyclopentadiene [179, 180].

See also [161, 165, 178, 264]

5. Hydrogenation of Arenes and Heterocyclic Compounds

Anthracene is hydrogenated to 1,2,3,4-tetrahydroanthracene by H-transfer from iPrOH at 75°C with $H_4Ru(PPh_3)_3$ or $H_2Ru(PPh_3)_4$ as catalyst. 1,2-dihydroanthracene is an intermediate of the reaction. PPh_3 and even N_2 decrease the activity of the catalyst [181].

Selective hydrogenation of the polynuclear heteroaromatic compounds (63)-(68) could be achieved under mild conditions (85°C, 21 bar) with $Rh(PPh_3)_3Cl$ as catalyst. In all cases saturation of the ring containing the heteroatom was observed [182].



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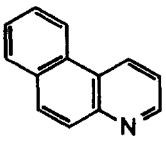

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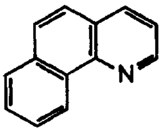

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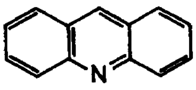

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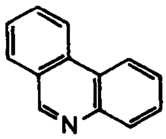

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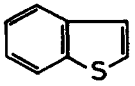
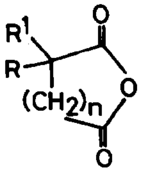


68

Unsaturated, aromatic and heterocyclic compounds like furan, 1,4-benzodioxane, 1-hexene, 1,5-cyclooctadiene, and PhR (R = H, NO_2, NH_2, OH) were successfully hydrogenated on catalysts composed of Pt, Pd, Ni, or Rh complexed with styrene-maleic acid or methyl methacrylate-maleic acid copolymer or polyacrylic acid [183]. A Pt complex catalyst was prepared by the reaction of silica-supported poly(γ-diphenylphosphinopropylsiloxane) with chloroplatinic acid. The catalytic activity of the complex in the hydrogenation of aromatic compounds was greatly affected by the P/Pt ratio [184].

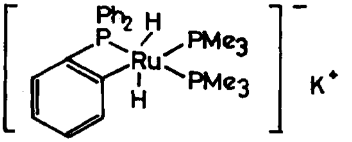
6. Hydrogenation of Carbonyl Compounds

The electrochemical reduction of aromatic ketones in DMF in the presence of Fe(II) salts was studied [185]. Esters of dicarboxylic acids are hydrogenated to hydroxy esters with $H_4Ru_4(CO)_8(PBu_3)_4$ as catalyst precursor at 180°C and 100-150 bar. The reaction is rather slow and several days are required to achieve significant conversions. The reactivity of the substrates decreases with increasing distance of the two ester groups, dimethyl glutarate is already unreactive and among the phthalic acid Me esters only the ortho isomer could be hydrogenated. This latter compound gives phthalide and methyl benzoate as products [186]. Hydrogenation of $PhCOCF_3$ is catalyzed by $H_2Ru(PPh_3)_4$ and $HRh(PPh_3)_4$. The Ru complex is also active in transfer hydrogenation with iPrOH or EtOH as H-donors. The corresponding Ru and Rh alcoholates which are intermediates of the catalytic reaction have been prepared [187]. Hydrogenation of unsymmetrically substituted cyclic anhidrides (69) (R = $CHMe_2$, Ph, R^1 = H, n = 1; R = Me, R^1 = H, Me, n = 1,2) catalyzed by Ru complexes with mono-, di-, or triphosphine ligands produced the isomeric lactones. Regioselectivity was influenced by the bulkiness of the substituent(s) on the anhydrides and on the phosphine ligands of the catalyst [188].



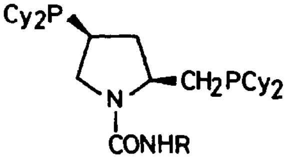
69

Catalytic analogs of $LiAlH_4$, the hydridophosphineruthenates (70), $K_2[(Ph_3P)_3(Ph_2P)Ru_2H_4]$, and $K[(Ph_3P)_3RuH_3]^{2-}$, prepared by reduction of Ru phosphine complexes are very active homogeneous hydrogenation catalysts for polar organic compounds like ketones, aldehydes, nitriles, and esters [189]. The ability of these new Ru hydride catalysts to promote hydrogenation of such polar double bonds is attributed to their anionic nature [190].



70

A new preparative method was developed for the transformation of the diphenylphosphinoyl groups of chiral diphosphines into the corresponding dicyclohexylphosphinoyl groups. Chiral diphosphines of the type (71) have been prepared in this way and used as ligands in the asymmetric hydrogenation of α-dicarbonyl compounds (72,73) to α-hydroxy carbonyl compounds with Rh(I) catalysts. Optical yields were moderate [191].



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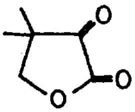

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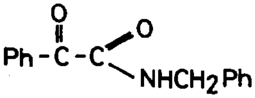
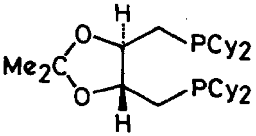


73

The same method was used for the preparation of the cyclohexyl analogues (74,75) of (-)-DIOP and (S,S)-Chiraphos. These new chiral diphosphines were also tested for the hydrogenation of (72) and (73), giving somewhat higher optical yields than (71) [192].



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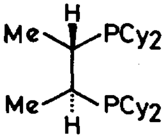


75

Kinetic investigation of the hydrogenation of aldehydes in the presence of a Rh complex-tertiary amine catalyst system, under hydroformylation conditions showed that the optimum CO pressure increases with increasing concentration of amine. This was attributed to a competitive coordination of CO and amine on the catalytically active Rh complex [193].

See also [202].

7. Hydrogenation of Nitro Compounds

Complexes of Re(V) with thiourea, N,N-ethylenethiourea, 2-benzimidazolethiol, and 1-methylimidazole-2-thiol are soluble catalysts for the hydrogenation of $PhNO_2$. Their activity and stability increases in the stated ligand order [194].

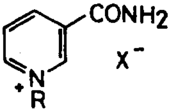
Reduction of nitrobenzene could not be performed under phase -transfer conditions with CO in benzene/5M NaOH and a catalytic amount of $Co_2(CO)_8$ or $Rh_2(HD)_2Cl_2$. The use of both metal compounds as catalysts resulted, however, in the reduction to aniline. The binuclear complex $Co(CO)_4Rh(CO)_2Cl^-$ may be the active catalyst in the reduction process [195]. The cobaloxime catalyzed hydrogenation of nitrobenzene gives azoxybenzene as the first detectable intermediate [196].

The complexes trans-$Pd(py)_2X_2$ (X = Cl, Br, I) catalyze the hydrogenation of nitroaromatics at 30°C even under normal pressure. Aldehydes, olefins and aliphatic nitro compounds are not reduced. The chloro complex is the most active [197]. The hydrogenation of $PhNO_2$ by hydrogen in the presence of $NaBH_4$ and Na(PdLCl) or PdL'Cl [H_2L = 4-(2-pyridylazo)resorcinol, HL' = 1-(2-pyridylazo)-2-naphthol or 1-(1-(2-hydroxynaphthyl)azo)-4-sulfobenzene] was studied [198].

Palladium or rhodium complexes supported on layered Zr(IV)-phosphonate were used as catalyst for hydrogenation of nitro-, cyano- and acetylenic groups or for the hydroformylation of propene [199]. Hydrogenation of aromatic nitro compounds by a silica supported poly(vinylpyrrolidone)-Pd complex was studied at room temperature and atmospheric pressure. The catalyst stability was increased by the addition of equimolar HOAc [200]. A polymer-bound Pd catalyst was prepared by attaching anthranilic acid to chloromethylated polystyrene and treating the polymer with $PdCl_2$. The catalyst can be used for the hydrogenation of aromatic nitro compounds at 60-90°C and 30-100 bar. It has a long lifetime and may be handled in air [201]. Methacrylic acid and divinylbenzene were copolymerized in the presence of SiO_2 and the silica-supported polymer treated with $PdCl_2$ or H_2PtCl_6. The Pd and Pt complexes prepared in this way catalyzed the hydrogenation of nitro compounds, alkenes, aldehydes, and ketones [202].

8. Miscellaneous Hydrogenations

N-Benzylideneaniline is hydrogenated to N-benzylamine with $Fe(CO)_5$ as catalyst in alcohol solution at 150°C and 100 bar H_2. The $HFe(CO)_4^-$ anion is regarded as the catalytically active species. In a stoichiometric reaction $H_2Fe(CO)_4$ hydrogenates the Schiff base rapidly at room temperature [203]. Using catalysts prepared *in situ* from $[Rh(NBD)Cl]_2$ and chiral diphosphines of the type $Ph_2PCHRCH_2PPh_2$ (R = Ph, iPr, $PhCH_2$) optical yields above 60% were achieved in the hydrogenation of the Schiff base $PhMeC{=}NCH_2Ph$, but the reproducibility of the results was poor [204]. Catalytic or stoichiometric reduction of pyridinium salts (76) by Co(I) complexes of Hdmg gave 1,4-dihydropyridines (77) with high regioselectivity. The isolation of a substituted tetrahydrobipyridine suggested that a dihydropyridyl cobalt complex was the reactive intermediate [205].



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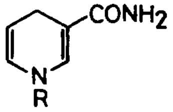


77

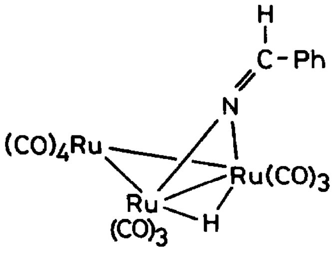
N,N-Dialkyl formamides can be hydrogenated to the corresponding methylamines using homogeneous catalysts derived from a variety of group 8 metal (Ru, Os, Rh, Ir and Fe) carbonyl cluster catalyst precursors at 220°C and about 100 bar (H_2:CO = 16:1):

$$R_2NCHO + 2\ H_2 \longrightarrow R_2NCH_3 + H_2O$$

The reaction is rather sluggish, turnover numbers do not exceed 100 moles product/moles catalyst day [206].

9. Coordination Chemistry Related to Hydrogenation

Reaction of $Ru_3(CO)_{12}$ with PhCN and H_2 at 130°C yields (78), a complex of PhCH=NH, which is a partially hydrogenated derivative of PhCN. Further treatment of this complex with H_2 results in (79). These reactions model some possible steps of the hydrogenation of benzonitrile on a metal surface [207].



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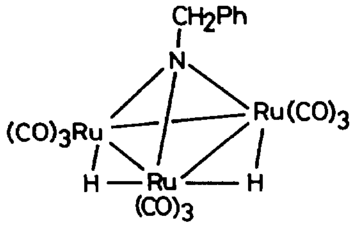


79

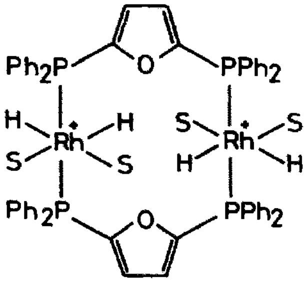
The rate of dehydrogenation of $HCo(CN)_5^{3-}$ to $Co(CN)_5^{3-}$ and the equilibrium between the two species was studied at different ionic strengths in water solution. The profound influence of cations is explained by the formation of ion pairs which by reducing the overall charge of the Co species promote dimerization [208].

The kinetics of the stoichiometric hydrogenation with $H_2Rh(PPh_3)_3Cl$ has been studied with different olefins and the results support the following mechanism:

$$H_2Rh(PPh_3)_3Cl \quad \overset{K}{\xrightleftharpoons[PPh_3]{\text{olefin}}} \quad H_2Rh(\text{olefin})(PPh_3)_2\,Cl \quad \xrightarrow{k}$$

$$\xrightarrow{k} \quad HRh(\text{alkyl})(PPh_3)_2Cl \quad \xrightarrow[PPh_3]{\text{fast}} \quad Rh(PPh_3)_3Cl + \text{alkane}$$

The values of K for substituted styrenes increase with the electron withdrawing power of the <u>para</u> substituent and the values of the intramolecular migratory insertion rate constant k follow the reverse trend [209]. Application of DANTE techniques to $H_2Rh(PPh_3)_3Cl$ reveals that the bis(phosphine) intermediate reacting with olefins in the catalytic cycle of hydrogenation probably contains the two PPh_3 ligands in cis position [210]. The binuclear complex (80) hydrogenates 3,3-dimethyl-1-butene in a stoichiometric reaction significantly slower than its mononuclear analogue (81) [211].



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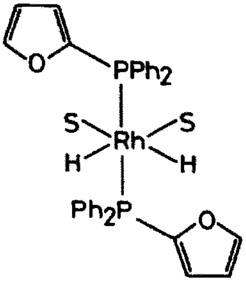


81

S = MeOH

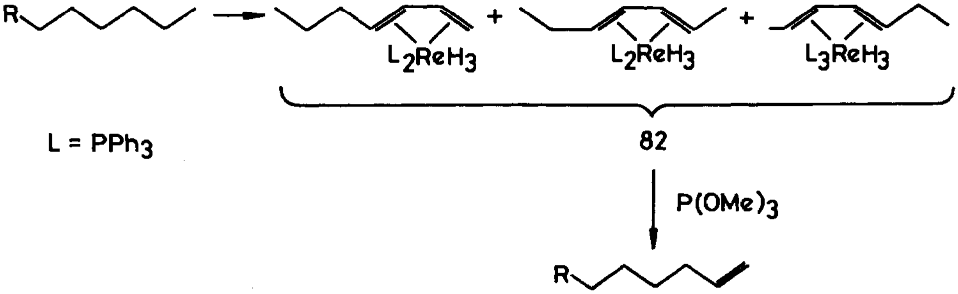
The structure of $[H_2Ir(Me_2CO)(PPh_3)_2]BF_4$, an active catalyst for the dehydrogenation of alkanes or alkenes, was determined [212]. A general method for the distinction between homogeneous and heterogeneous hydrogenation catalysts has been developed. Soluble and cross-linked polymers containing olefinic double bonds and aromatic rings were prepared and it was found that they are hydrogenated in the presence of soluble catalysts whereas heterogeneous catalysts are ineffective. Using this test, $[Ir(COD)(PPr^i_3)py]PF_6$ and $Rh_2(C_5Me_5)_2Cl_4$ were found to behave as a homogeneous olefin hydrogenating catalysts, but the Rh complex acted like a heterogeneous catalyst in the hydrogenation of aromatic rings [213].

Several Pd complexes of anion exchangers were studied by ESCA and the results compared with the catalytic activity of these complexes for hydrogenation. Pd complexes with OH forms of ion exhangers exhibited highest activity [214].

$(Et_3P)_2Pt(neopentyl)_2$ reacts with H_2 and yields $(Et_3P)_2PtH_2$ and neopentane. In the absence of Et_3P the rate limiting step is the dissociation of Et_3P from the complex. In the presence of Et_3P the rate of reaction depends on the first order of H_2 pressure and either addition of H_2 to Pt or more probably elimination of neopentane from Pt becomes rate limiting [215].

10. Dehydrogenation

Photocatalytic dehydrogenation of iPrOH proceeds in the presence of $(NH_4)_6Mo_7O_{24}.4H_2O$. A reduced Mo species is also formed which was characterized spectroscopically [216]. n-Alkanes (C_6-C_8) react at 70°C with $H_7Re(PPh_3)_2$ and 3,3-dimethylbutene to afford equilibrium mixtures of the corresponding (diene)-rhenium trihydride complexes (82). These latter are transformed by $P(OMe)_3$ at 60°C into 1-alkenes [217]:



H_2 is produced catalytically, on photolysis of aqueous solutions of ascorbic acid in the presence of $[Ru(bpy)_3]^{2+}$ and $HPd(PEt_3)_3$. Photochemically produced $[Ru(bpy)_3]^+$ transfers an electron to the Pd complex from which H_2 is evolved. The organic product is dehydroascorbic acid [218].

Primary alcohols are transformed at 145°C into esters in the presence of a hydrogen acceptor (A) and $Ru_3(CO)_{12}$ as catalyst precursor according to the following stoichiometry:

$$2\ RCH_2OH + 2\ A \longrightarrow RCOOCH_2R + 2\ AH_2$$

Acetylenes, olefins and aldehydes or ketones may serve as hydrogen acceptors, the best results were achieved with cyclohexanone in the presence of a small amount of diphenyl acetylene. The reaction takes place in two steps: in the first, alcohol is dehydrogenated to aldehyde and in the second, aldehyde and alcohol react and are dehydrogenated to form the ester. This latter reaction also requires the presence of the hydrogen acceptor [219].

Ziegler catalysts prepared from Co or Ni acetylacetonate and iBu_3Al or iBu_2AlH catalyze the dehydrogenation of tetraline to naphthalene at 150-200°C. Phosphines inhibit the reaction [220].

Homogeneous catalytic dehydrogenation of cyclooctane to cyclooctene has been effected by means of a variety of Ir and Ru polyhydrides at 150°C, in the presence of 3,3-dimethylbutene as H--acceptor. Best results (45-70 catalytic turnovers in several days) have been achieved with $H_5Ir(PPr^i_3)_2$, $H_5Ir[P(C_6H_5F\text{-}p)_3]_2$ and

$H_4Ru[P(C_6H_5F\text{-}p)_3]_3$. The reaction mixtures turned gradually brown but appeared to be perfectly homogeneous [221]. Liquid-phase dehydrogenation of iPrOH to acetone proceeds under visible light irradiation with (TPP)RhCl as catalyst. A bimolecular reaction between (TPP)RhH complexes in the photoexcited and ground states is involved in the photocatalytic cycle [222]. This bimolecular process was studied also quantum chemically to describe the process of H-H bond making and Rh-H bond breaking. Two molecular orbitals were designated as important: the symmetric pair of unoccupied orbitals with H-H bonding and Rh-H antibonding phases and the symmetric pair of occupied orbitals with both H-H and Rh-H bonding phases [223]. Photogeneration of H_2 from iPrOH can be achieved with $Rh(PPh_3)_3Cl$ and a number of other Rh(I) complexes after exposure to air. $RhCl_3.3H_2O$ + PPh_3 is less active under these conditions [224].

β -Amino ketones are dehydrogenated by $PdCl_2(MeCN)_2$ in the presence of Et_3N in a stoichiometric reaction to give α , β -unsaturated aminoketones [225]:

See also [334, 373]

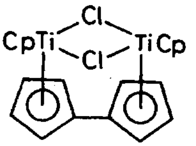
11. Hydrogen Transfer Reactions

a) Alkanes as Hydrogen Donors

Complexes of the type $[H_2Ir(Me_2CO)_2L_2]SbF_6$ [L = PPh_3 or $(p\text{-}FC_6H_4)_3P$] in the presence of tBuCH=CH_2 at 85-150°C can aromatize cyclohexanes to arenes in good yields. In the presence of a base cyclooctane is dehydrogenated to cyclooctene [226].

b) Hydrogenation of C=C bonds

The dimeric titanocene (83) catalyzes the intermolecular H-transfer in unsaturated hydrocarbons. Cyclic hydrocarbons disproportionate into saturated and aromatic hydrocarbons while linear olefins yield predominantly linear alkanes and high molecular weight tar [227].

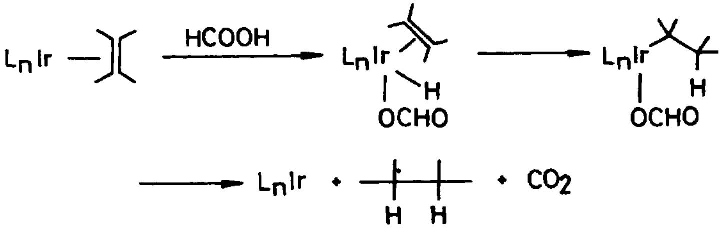


83

Cocondensation of chromium atoms with cyclohexene or 4-methylcyclohexene-1 results in hydrogenations and dehydrogenations to the corresponding cyclohexanes and aromatic hydrocarbons [228]. The mechanism of the transfer hydrogenation of 1-hexene with iPrOH as H donor and trans-Mo$(N_2)_2$(dppe)$_2$ has been studied. The stoichiometric reaction of 1-hexene with MoH_4(dppe)$_2$ suggests that the active species in transfer hydrogenation is MoH_2(dppe)$_2$ which is formed from the catalyst precursor by its reaction with iPrOH [229].

Kinetic investigation of the Ru_2[(-)-DIOP]$_3Cl_4$ -catalyzed transfer hydrogenation of unsaturated acids and esters by alcohols indicated that the catalytically active species is Ru[(-)-DIOP]Cl_2. This species coordinates the substrate and H-transfer takes place within the complex [230].

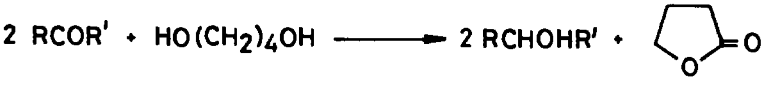
Polystyrene-bound IrCl(CO)$(PPh_3)_2$ promotes H-transfer from formic acid to a variety of olefinic substrates. Detailed kinetic studies were carried out with benzylideneacetophenone as H-acceptor. The essential steps of the mechanism as proposed are illustrated below:



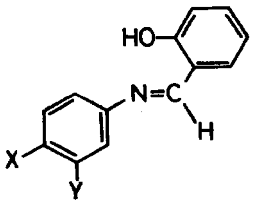
The fully activated catalyst is air stable and essentially leach proof [231]. Transfer hydrogenation of the olefinic double bond of α, β-unsaturated ketones by formic acid is efficiently catalyzed by Ir(CO)$(PPh_3)_2$Cl reacted with a diphenylphosphinated 0.02 cross-linked styrene-divinylbenzene copolymer. The anchored catalyst is more reactive than the homogeneous complex [232].

c) Hydrogenation of C=O Bonds

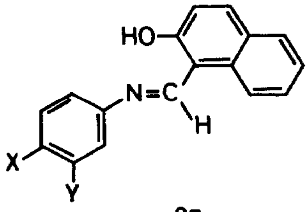
Aldehydes and ketones can be reduced to alcohols with high yields by transfer hydrogenation using 1,4-butanediol as H-donor and ruthenium-phosphine complexes like $HRuCO(PPh_3)Cl$ as catalysts. No solvent has to be used and the conversion is not limited by equilibrium as it is in the case of secondary alcohols as H-donors because the diol is transformed into γ -butyrolactone [233]:



The thermally inert complex $HCo[PPh(OEt)_2]_4$ catalyzes the hydrogen transfer from secondary alcohols to ketones under irradiation. The active species is probably coordinatively unsaturated $HCo[PPh(OEt)_2]_3$ [234]. Catalyst systems prepared in situ from $Rh_2(COD)_2Cl_2$, KOH, and bidentate phosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1-4) proved to be active in the transfer hydrogenation of alkylcyclohexanones with refluxing iPrOH. Mainly <u>cis</u> alcohols were formed [235]. A similar stereoselectivity was observed if PPh_3 or PBu_3 were used as ligands [236].

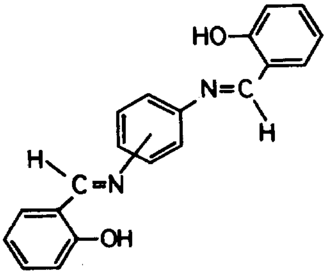


84

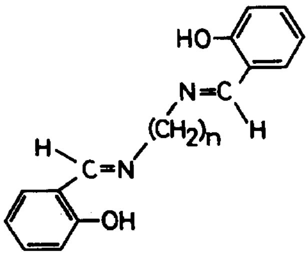


85

X = MeOH, H
Cl, NO_2
Y = H, Cl



86 (o-, m-, and p- isomers)



87

n = 2,3

H-transfer reactions from iPrOH to acetophenone or cyclohexene are catalyzed by neutral Rh(I) complexes of the type Rh(COD)L and $Rh_2(COD)_2L'$ in the presence of KOH. L (84,85) and L' (86,87) are Schiff base ligands. The catalytic activity of these systems is lower than that of related cationic ones [237].

Transfer hydrogenation of aldehydes and ketones by sodium formate under phase-transfer conditions takes place according to the following equation:

$$RR'CO + HCOONa + H_2O \longrightarrow RR'CHOH + NaHCO_3$$

$Ru(PPh_3)_3Cl_2$ was found to be the best catalyst for aldehyde reduction and a 1:10 mixture of $Rh(PPh_3)_3Cl$ and PPh_3 showed the highest activity in the transformation of ketones [238]. Complexes of the type $[Ir(HD)(L)ClO_4]$ (L = substituted phenanthroline ligands) catalyze the H-transfer from cyclopentanol to 4-tert-butylcyclohexanone following pseudo first order kinetics. The covalent analogues Ir(HD)(L)X (X = Cl, Br, I) are less effective catalysts [239]. Transfer hydrogenation of ketones and aldehydes by methanol as donor is catalyzed at temperatures around 150°C by C_5Me_5 complexes of Rh and Ir, $OsH(Br)CO(PPh_3)_3$, and $Ru(PPh_3)_3Cl_2$. MeOH is transformed into methyl formate, and the reduction thus may be described by the equation

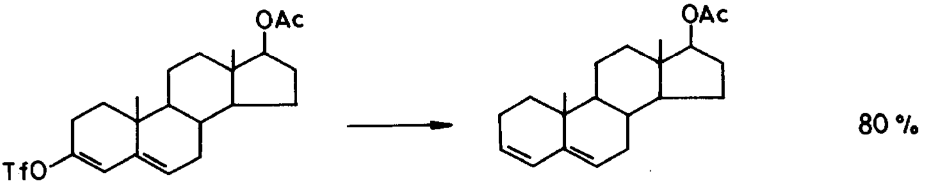
$$2\ R_2CO + 2\ CH_3OH \longrightarrow 2\ R_2CHOH + HCOOCH_3 \qquad [240]$$

The iridium complexes $[Ir(COD)L_2]^+$ (L = tertiary phosphine) are very active catalysts for the transfer hydrogenation of cyclohexanone and 4-tBu-cyclohexanone with iPrOH. At the start of the reaction turnover numbers above 1000 s^{-1} can be observed, tha catalyst is, however, rapidly deactivated [241]. The system formed in situ from $Ir_2(COD)_2Cl_2$ and $P(C_6H_4OMe-\underline{o})_3$ catalyzed the selective (90%) transfer hydrogenation of the carbonyl group in 5-hexen-2-one by iPrOH. The yield of unsaturated alcohol increased with the P/Ir ratio. Other phosphines and unsaturated alcohols tested gave less satisfactory results [242].

See also [187].

d) Hydrogenolysis by Hydrogen Transfer

Enol triflates like (88) may be reduced with formic acid and tributyl amine (tributylammonium formate) in the presence of $Pd(OAc)_2(PPh_3)_2$ as catalyst at 60°C in DMF to the corresponding alkenes (89). A valuable feature of the method is the regioselective and quantitative introduction of a D atom if DCOOD is used [243].



88 89

The complex $Rh_2(CO)_2(PBu^t_3)_2$ (μ-Cl)[μ-$SCH_2CH_2Si(OEt)_3$] fixed on a fused silica support was used as catalyst for the transfer hydrogenation of α, β-unsaturated ketones with formic acid and the transfer hydrogenolysis of trihalomethyl compounds with iPrOH [244]:

$$\underset{\substack{|\\ OH}}{PhCHCCl_3} + Me_2CHOH \longrightarrow \underset{\substack{|\\ OH}}{PhCHCHCl_2} + Me_2CO + HCl$$

12. Reduction without Molecular Hydrogen

a) Transition Metal Hydrides

Acyl chlorides can be selectively reduced under mild conditions to the corresponding aldehydes by group 6B anionic hydrides $HM(CO)_4L^-$ (M = Cr, W; L = CO, PR_3). The reaction is nearly quantitative. In the presence of acid the aldehydes consume a second equivalent of hydride and are reduced to alcohols. Alkyl bromides or nitro aromatics do not interfere with the reaction [245]. Group 6 anionic deuterides $DM(CO)_5^-$ (M = Cr, W) may be conveniently used as deuterium-transfer reagents for the reduction of organic halides. The deuterides are generated in situ from the corresponding hydrides by exchange with MeOD [246]:

$$R\text{-}Br + HM(CO)_5^- \xrightarrow[THF]{MeOD} R\text{-}D$$

$HFe(CO)_4^-$ supported on an anion exchange resin (Amberlyst A26) reduces acid chlorides to the corresponding aldehydes in THF at reflux temperature [247].

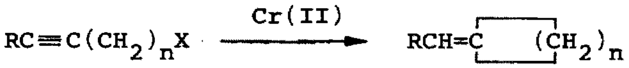
The completely regioselective reduction of 1-acylpyridinium salts (90) to 1-acyl-1,4-dihydropyridines (91) was achieved by a copper hydride reagent prepared from $LiAlH(OBu^t)_3$ and CuBr [248].

90 91

See also [203,209,211].

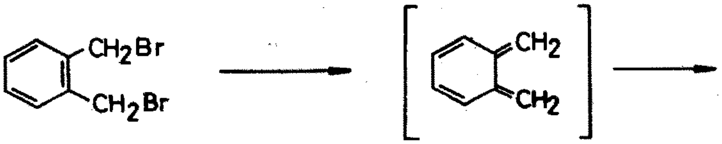
b) Low Valent Transition Metal Complexes

Amine N-oxides were reduced to amines with $TiCl_3$ in over 60% yield [249]. Aldehydes or ketones were reduced to alcohols and hydrocarbons by $Cp_2Ti(CO)_2$ in refluxing THF. Some aromatic carbonyl compounds yielded also reductive coupling products like olefins or pinacols [250]. Reduction of halides of the type $RC{\equiv}C(CH_2)_nX$ with Cr(II) in aqueous DMF containing ethylenediamine yields in the $n = 4$ and $n = 5$ cases substituted methylenecycloalkanes:



$$RC{\equiv}C(CH_2)_nX \xrightarrow{Cr(II)} RCH{=}C\;(CH_2)_n$$

Experimental conditions which favor longer lifetimes for the intermediate radicals result in increased cyclization [251]. On treatment with chromous chloride, α,α-dibromo-*o*-xylenes (92) undergo reductive elimination affording *o*-quinodimethanes (93) which either spontaneously dimerize or may be trapped with dienophiles [252].



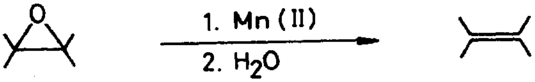
92 93

Benzenethiosulfonate (94) is reduced by $(NH_4)_2(Mo_2S_{12})$ to diphenyldisulfide in refluxing acetonitrile with 81% yield. The same product is formed from benzene sulfonyl chloride presumably by oxidative coupling followed by reduction [253].

$$\underset{94}{PhSO_2SPh} \longrightarrow PhSSPh$$

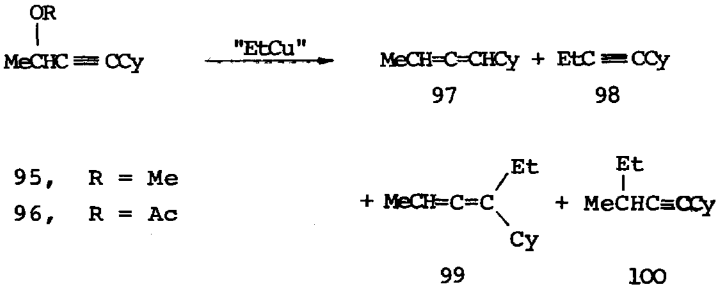
$$2\ PhSO_2Cl \longrightarrow PhSSPh$$

Alkyl-Mn(II) compounds (prepared in situ) deoxygenate epoxides to olefins:



MeMnCl or Bu_3MnLi are used as reductants the latter being the more reactive reagent [254].

Propargylic methyl ethers (95) and acetates (96) were transformed with an ethyl cuprate, derived from EtMgBr and $CuBr.Me_2S$ into reduction (97,98) and substitution (99,100) products. The methyl esters gave rise to more reduction products than the acetates [255].



95, R = Me
96, R = Ac

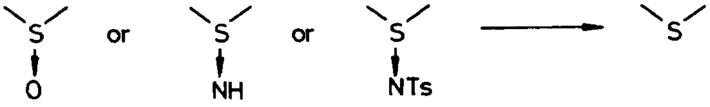
c) Inorganic Reductants in the Presence of Transition Metal Complexes

Alkenyl sulfides were reduced to the corresponding alkyl sulfides with $HSiEt_3$ in the presence of $TiCl_4$ with good yields.

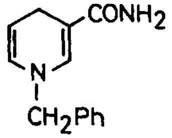
The reduction proceeds through the formation of an alkyltitanium intermediate [256].

Systems composed of molybdate and thiol ligands such as L-cysteine or aminoethanethiol are effective catalysts for the reduction of hexynes to the corresponding hexenes and hexane by $NaBH_4$ [257].

Reduction of sulfoxides, sulfilimines (101) and p-toluenesulfonyl-sulfilimines (102) by $NaBH_4$ or 1-benzyl-1,4-dihydronicotinamide (BNAH, 103) is catalyzed by Fe(TPP)Cl or Co(TPP). Best results were obtained with the Fe(III)(TPP)/BNAH system [258].

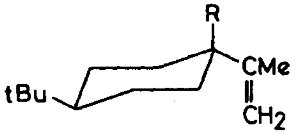


101 102



103

Olefins (104) and (105) were reduced with Zn + AcOH and catalytic amounts of cob(I)alamin. If reduction was slow the catalyst was able to differentiate the two diastereotopic faces of the endocyclic double bond in (105) [259].



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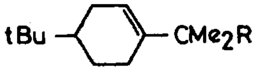
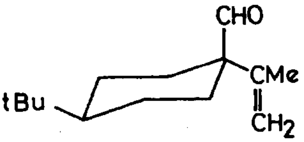


R = CN, CH_2OH

105

Cob(I)alamin also catalyzed the reduction of aldehyde (106) with Zn + AcOH to the cyclopropanols (107) and (108) [260].



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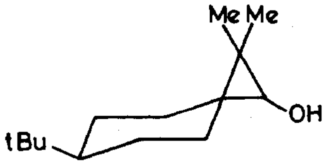

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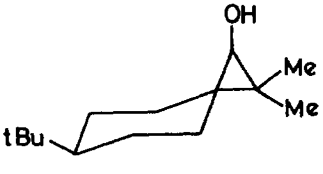

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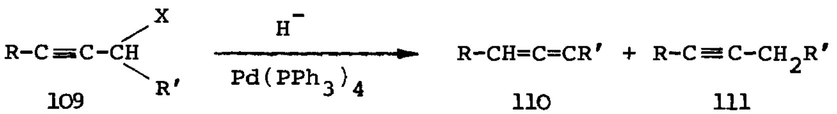
Alkenes can be hydrogenated using $NaBH_4$ in the presence of $CoCl_2$ in a mixed THF + MeOH solvent. If only THF is used as solvent, hydroboration is the main reaction [261]. The reduction of aryl-substituted ketones with Et_4NBH_4 is catalyzed by Co(TPP) under the influence of visible light. Deuterium labeling experiments show that the H of the BH_4^- anion is directly transferred to the α-carbon atom [262]. Reduction of nitrosobenzene with carbon monoxide was carried out in the presence of Rh(I) or Ru(II) nitrosobenzene complexes as catalyst. In ethanol the reduction proceeded already at 75°C and 1 bar, in benzene more drastic conditions were needed. Azoxybenzene was the main product but a wide range of other compounds was also formed [263].

Complexes of polyethyleneimine with $PdCl_2$, $RhCl_3$, $NiCl_2$, $CoCl_2$ and $RuCl_3$ catalyze the hydrogenation of 1,3-cyclohexadiene with H_2 or $NaBH_4$. The order of activity of the metals is Pd > Rh > Ru > Ni,Co [264]. Reduction of propargylic halides or esters (109) to allenes (110) with hydride donors in the presence of Pd(0) proceeds best if Et_3BHLi is used for the reduction of mesylates:



$$\text{R-C}\equiv\text{C-}\overset{\text{X}}{\underset{\text{R}'}{\text{CH}}} \xrightarrow[\text{Pd(PPh}_3)_4]{\text{H}^-} \text{R-CH=C=CR}' + \text{R-C}\equiv\text{C-CH}_2\text{R}'$$

109 110 111

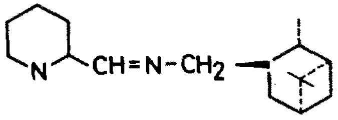
R′ = Br, OMs

Acetylenes (111) are formed as byproducts [265].

The combination of $NaBH_4$ with $NiCl_2.6H_2O$ converts unsaturated oximes into saturated amines. If the reduction is carried out in the presence of MoO_3 the C=C double bond remains intact [266]. Aromatic and aliphatic nitro compounds are reductively N-acylated by carboxylic acids to N-substituted amides at 180° in the presence of a catalytic amount of $Pt(PPH_3)_2Cl_2$ combined with $SnCl_4$, under 60 bar CO pressure. Instead of $SnCl_4$ other Lewis acids like $FeCl_3$ or $AlCl_3$ may be used [267].

d) Reduction of Carbonyl Compounds via Hydrosilylation

Hydrosilylation of acetophenone with Ph_2SiH_2 was investigated using 37 different chiral N-chelating ligands in combination with $Rh_2(COD)_2Cl_2$ or $K[PtCl_3(C_3H_4)]$ as catalysts or performing the reaction in the presence of 21 different Rh or Pt complexes already containing these ligands. Some of the ligands used are shown below (109-112). Enantioselectivity of the catalysts was characterized by determining the optical purity of α-phenyl ethanol obtained after hydrolysis. Highest o.y. was 79% obtained with (109) and rhodium [268].



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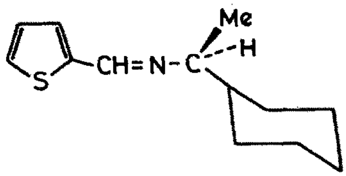

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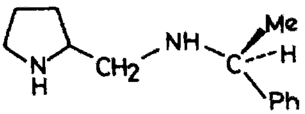

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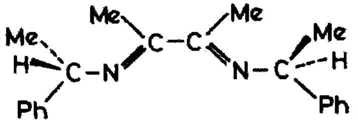

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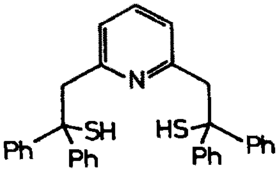
e) Organic Reductants in the Presence of Transition Metal Complexes

The oxomolybdenum complex MoO(L)(DMF) (LH_2 = 113) catalyzes the reduction of Me_2SO by PPh_3:

$$Me_2SO + PPh_3 \longrightarrow Me_2S + PPh_3O$$

This system models the mononuclear active site of certain molybdoenzymes that catalyze oxygen atom transfer reactions [269].



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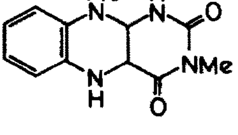
Various nitroarenes having chloro, methyl or methoxy substituents were reduced at 125-180°C to the corresponding aminoarenes in high yields using formic acid in the presence of $Ru(PPh_3)_3Cl_2$ as catalyst. Heterocyclic compounds such as quinoline, indole, and quinoxaline could also be reduced under such conditions [270]. $RuCl_2(dpm)_2$ catalyzes the reduction of 1-hexene, 1-heptene and allylic alcohol by $HCO_2H + HCO_2Na$ in water at 25-30° to give the saturated products in high yields. The reaction is less efficient with cyclohexene and PrCHO [271]. The reduction of $p\text{-}ClC_6H_4NO_2$ with the reduced flavin (114) in EtOH under anaerobic conditions is accelerated by divalent metal ions ($Co^{2+} > Ni^{2+} > Mn^{2+}$) which act by flattening the 1,5-dihydroflavin molecule via coordination at the C=O(4) and N(5) positions [272].



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α, β-Unsaturated carbonyl compounds are reduced to the corresponding saturated carbonyl compounds by N-propyl-1,4-dihydronicotinamide (an NADPH model compound) with the aid of $Rh(PPh_3)_3Cl$.

The reduction was accelerated by the addition of an equivalent amount of $LiClO_4$. The system is ineffective for the reduction of α,β-unsaturated esters [273]. Aryl iodides are reduced to the corresponding arenes with N-benzyl-1,4-dihydronicotinamide (also a model of NADPH) in the presence of $Rh(PPh_3)_3Cl$ as catalyst. Nitro, carbonyl, and ester functions are inert under these conditions. The method is also applicable for the reduction of vinyl halides [274]. Dimethyl diazomalonate smoothly deoxygenates epoxides to alkenes with $Rh(OAc)_2$ as catalyst in toluene solution at reflux temperature:

Yields are above 75% [275].

Aryl bromides are conventiently dehalogenated with benzyl alcohol and NaOH in a two-liquid phase system in the presence of $Pd(PPh_3)_2Cl_2$:

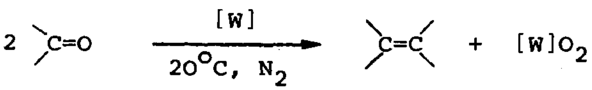
$$ArBr + PhCH_2OH + NaOH \longrightarrow ArH + PhCHO + NaBr + H_2O$$

Phase transfer catalysts significantly enhance the rate of the reaction [276]. Terminal allylic compounds like allylic esters, phenyl ethers, carbonates, chlorides and vinyl epoxides are hydrogenolyzed by ammonium formate to give 1-alkenes by using $PdCl_2$ + PBu_3 (Pd:P = 1:4) as catalyst [277]:

X = OAc, OPh, OCOOMe, Cl.

f) Electroreduction

Carbonyl compounds are reductively dimerized into olefins by chemically or electrochemically reduced tungsten species:



$$2\ \rangle C{=}O \xrightarrow[20^{\circ}C,\ N_2]{[W]} \rangle C{=}C\langle + [W]O_2$$

Best results are obtained by means of a controlled potential electroreduction of WCl_6 at a Pt electrode. Benzaldehyde gives stilbene quantitatively (mainly E) when THF is used as the solvent and Al as the anode. When PhCHO is added after the electroreduction of WCl_6, yield of stilbene is very low, however [278]. The electrochemical reduction of allyl halides to 1,5-hexadiene is catalyzed by $Ni(PPh_3)_4$ which is cathodically generated and continuously recycled [279]. Electroreductive cleavage of allylic acetates into alkenes is catalyzed by $Pd(PPh_3)_4$. The method can also be used for the conversion of allylic esters into the corresponding carboxylic acids [280].

If the electroreduction of allyl or benzyl bromides (R-Br) is carried out in the presence of $Cu(acac)_2$, the yield of reductive coupling products (R-R) is increased at the expense of hydrogenolysis products (R-H). Analogous chlorides or iodides are unaffected by the copper additive [281].

See also [185].

IV. Oxidation

1. Catalytic Oxidation of Hydrocarbons or Hydrocarbon Groups with O_2

a) General

The rate of oxidation of hydrocarbons at 90°C with O_2 in the presence of $Co(OAc)_2$ + NaBr decreases in the order m-xylene > toluene > n-paraffins > isooctane [282]. The relative rates for the oxidation of hydrocarbons using a cobalt-bromine catalyst were found to be olefins ≈ alkylaromatics > cycloalkanes > isoalkanes > n-alkanes [283]. The effect of Co^{2+}, Br^- and H_2O in cobalt-bromide complex catalysts on the oxidation of hydrocarbons was examined. Only the low Br^- containing complexes were found to be active. Water reduced the oxidation rate [284].

b) Oxidation of Alkanes

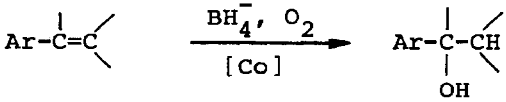
The oxidation of pentadecane at 110°C in the presence of a Cr stearate + Pb stearate catalyst mixture gave acids and ketones with up to 97% selectivity [285]. The selectivity in the oxidation of saturated hydrocarbons by O_2 in py + AcOH in presence of the soluble iron complex $[Fe(II)Fe_2(III)O(OAc)_6py_3]_2py$ and Zn is strongly dependent on the reaction conditions. Using air and slow stirring, adamantane is attacked almost exclusively at the secondary positions [286]. Oxidation of cyclohexane was investigated with mixtures of Al-, Co- and Cr-stearates as catalysts. Best results were obtained with Al + Co [287].

See also [389].

c) Oxidation of Olefins

The reactivity of alkenes in the catalytic oxidation to glycol esters at 135-170°C in carboxylic acid solvents using transition metal (Ti, Mn, Fe, Co, Ni, Cu) complexes as catalysts increased in the order $CH_2{=}CMeCH_2CMe_3$ < 1-heptene < cyclohexene [288]. The hydrozirconation and following oxidation of styrene gave both $PhCH_2CH_2OH$ and PhCHMeOH [289]. The liquid-phase oxidation of 1-nonene in the presence of cyanides of molybdenum (0, II, and IV) proceeds by two paths, one involving an intermediate catalyst-hydroperoxide complex and the other an intermediate catalyst-hydroperoxide-substrate complex [290]. The rate of 1-nonene oxidation increases in the order of catalysts $K_4[Mo(CN)_8] < K_4[MoO_2(CN)_4] < K_4[MoO(CN)_4] < K_4[Mo(CN)_4]$ [291]. The catalytic activity of group VI transition metal carbonyls in the autoxidation of methyl oleate and decomposition of Me oleate hydroperoxide at 80°C to form epoxy and hydroxy compounds increases in the order $W(CO)_6 < Mo(CO)_6 < Cr(CO)_6$ [292]. The oxidation of substituted olefins with O_2 using a [tetrakis(p--methoxyphenyl)porphin]MnCl + $NaBH_4$ catalyst system has been studied. The rate and extent of oxidation increased with the degree of substitution at the double bond [293]. The oxidation of 2,3-dimethyl-2-butene, isobutene and 2-methyl-2-pentene gave regioselectively 2,3-dimethyl-2-butanol, tBuOH and 2-methyl-2-pentanol, respectively [294].

Oxidation of α-pinene by O_2 with Co-naphthenate as catalyst gives trans-verbenol and verbenone [295]. Cobalt ion-exchanged faujasites X have been treated with 1,2-dicyanobenzene or dimethylglyoxime. Co(phthalocyanine) and $Co(dmg)_2$ were formed and prefentially located within the cages of the faujasite network. The encaged Co complexes catalyzed the oxidation of propene to acetone, acetaldehyde and formaldehyde [296]. Aryl olefins can be transformed into benzylic alcohols by the use of O_2 and BH_4^- in the presence of a catalytic amount of Co(TPP):



Detailed investigation of the reaction with styrene as a substrate revealed that Co(TPP) catalyzed three elementary steps of the overall catalytic process: formation of α-phenyl ethylhydroperoxide, decomposition of the hydroperoxide into α-phenyl ethanol and acetophenone and reduction of acetophenone [297].

It was reported that $Rh_2(OAc)_4$ is an effective catalyst for the autoxidation of 1,4-cyclohexadienes to aromatic hydrocarbons, H_2O_2 and water, for the selective cleavage of 1-phenyl-1,3-butadiene to cinnamaldehyde and for the conversion of alkyl hydroperoxides to their corresponding alcohols and O_2 [298]. The mechanism of the $RhCl_3.3H_2O$-catalyzed oxidation of octene-1 to octanone-2 by O_2 in EtOH has been investigated using deuterated substrate and solvent. Substantial label exchange with the solvent was observed [299]. Oxidation of cyclohexene has been studied in the presence of Rh(I) complexes activated by cumyl hydroperoxide. The hydroperoxide eliminated the induction period. The main product was cyclohexenyl hydroperoxide [300]. The oxidation of α-pinene in an organic solvent at 65-80°C with $PdCl_2$ + $CuCl_2$ as catalyst gave verbenol or verbenone as the major products [301]. The same oxidation was also studied with added alkali and alkaline earth chlorides. Best yields of verbenone, verbenol and carvone were obtained with LiCl [302]. Heteropolyacids could be used as oxidants in the Wacker catalyst system. Among the combinations examined the $PdSO_4$ + $H_3PMo_6W_6O_{40}$ system showed the highest activity for the oxidation of cycloolefins to alicyclic ketones. The largest turnover with respect to Pd was 85 [303]. A mathematical model was developed for ethylene glycol monoacetate preparation by ethene oxidation in acetic acid solutions containing $PdCl_2$ and iron nitrate [304].

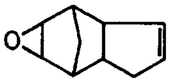
See also [305, 391].

d) Epoxidation of Olefins

In the liquid-phase oxidation of cyclohexene Co, Mn, Fe and Ce ions catalyze autoxidation, V and Mo ions catalyze epoxidation.

Epoxidation proceeds via two stages: autoxidation to form cyclohexene hydroperoxide followed by reaction with cyclohexene to form cyclohexene epoxide [305].

In the liquid-phase oxidation of dicyclopentadiene the ratio of the monoepoxides (115) : (116) increased from 2.6 (uncatalyzed) to 7.4 if $MoO_2(acac)_2$ was used as catalyst. In the latter case bisepoxide (117) formation was less than 10% [306]. Cobalt compounds and complexes increased the rate of oxidation [307].



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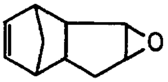

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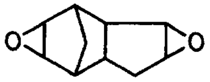

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The yields of epoxide formed in the autoxidation of *cis*- and *trans*- β-methylstyrene were not influenced by $MoO_2(acac)_2$, but in the case of the *cis*-olefin the Mo complex increased the *cis*:*trans*-epoxide ratio [308]. Olefins were epoxidized by a P-450 model catalytic system composed of H_2, O_2, collodial Pt and the Mn(III) complex of sulfonated tetraphenylporphin. Several hundred turnovers were achieved and polyolefins were almost exclusively monoepoxidized [309]. The liquid-phase oxidation of α -methylstyrene with air at 70-130°C yielding PhCOMe and α -methylstyrene oxide was first order in $PhCMe{=}CH_2$ and 0.5 order in AIBN initiator using $Co(OAc)_2$ catalyst. This Co salt was more effective in accelerating the autoxidation than $Mn(OAc)_2 + Na_2CO_3$ [310]. Optimal conditions were determined for the epoxidation of propene by O_2 in the presence of benzaldehyde and Co(*p*-MeTPP) as catalyst. Epoxidation is performed by the perbenzoic acid coordinated to Co [311].

See also [354].

e) Oxidation of Aromatics

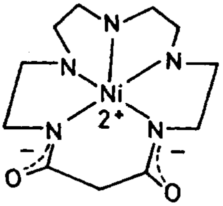
Several transition metal (Mn, Fe, Cu, Ag) polyphthalocyanines enhance the rate of cumene oxidation, but also decrease the selectivity to cumene hydroperoxide. Cumyl alcohol is the main by-product [312]. Addition of $Mn(OAc)_2$ inhibits CO_2 formation in the $CoBr_2$-catalyzed oxidation of p-xylene in AcOH. The inhibition results from reduction of Co^{3+} by Mn^{2+} [313].

Hydroxylation of substituted aromatics by O_2 was studied in the presence of Fe^{2+} and ascorbic acid. Reactivity varied only slightly with the substituent but an oxygen atom in the side chain significantly altered the relative amount of ortho, meta,and para monohydroxylated products [314].

Substituted toluenes were oxidized by air in AcOH, using Co acetate as a catalyst and NaBr or paraldehyde as a promoter. In most cases carboxylic acids and aldehydes were the main products of oxidation [315,316]. The rate of toluene oxidation by O_2 in AcOH with a cobalt bromide catalyst was increased by adding $HfOCl_2.8H_2O$ [317]. The liquid-phase oxidation of toluene at 75°C in the presence of $Co(OAc)_2$ and NaBr was accelerated by $CoCl_2$, the rate showed a maximum at a $Co(OAc)_2$:$CoCl_2$ ratio of 1:1 [318]. The simultaneous oxidation of xylene and methyl-p-toluate by O_2 in the presence of ionic Co compounds as catalysts was inhibited by p-cresol [319]. The liquid-phase oxidation of tetralin at 65-90°C catalyzed by a complex of $CoCl_2$ and polyurethane was first order in tetralin and 0.5 order in catalyst [320]. In the liquid-phase oxidation of xylene and durene in AcOH catalyzed by $CoBr_2$ and NaBr the tetrahedral complex anion $[CoBr_3(AcOH)]^-$ acts as catalyst. The activity of the anion is independent of the cation (in this case Na) [321]. Tetralin was oxidized using Co, Mn or Cu chloride complexes with ethylene glycol to determine the effects of polymer mobility and chain length on activity. In complexes containing one metal ion per polymer chain activity increased with chain length. Activity decreased with increasing number of metal ions per chain [322]. Kinetic data of the liquid-phase oxidation of tetralin to hydroperoxide on polyethylene glycol-$CoCl_2$ complexes fixed on silica gel showed that the reaction proceeds with the same mechanism as in the homogeneous reaction [323]. The rate of cumene oxidation on some Co complexes containing glycine, histidine,and O_2 ligands and anchored on SiO_2 decreased with increasing temperature, probably because of deoxygenation above 65°C [324]. Immobilized Co(II) acetate complexes showed a catalytic effect on oxidation of toluene at 80°C in AcOH when dioxane was added to the solution. Co(II) acted by promoting the transfer of oxygen from the peroxide formed by dioxane to PhMe [325]. The oxidation of aromatic hydrocarbons by O_2 in AcOH in the presence of $CoBr_2$ was studied by redoximetry and Br-selective potentiometry. The accumulation of Co(III) was noted [326].

Co^{3+}/Co^{2+} redox potential and O_2 consumption were synchronously recorded in the reaction mixture of the air oxidation of toluene to PhCOOH in acetic acid with a Co acetate bromide catalyst. [327].

Rate constants of the liquid-phase oxidation of tetralin in the presence of different Ni dioxime complexes were determined. The maximal accumulation of 1-tetralol occured with a catalyst containing dimethylglyoxime as an equatorial ligand [328]. Oxidation of benzene by $^{17}O_2$ at room temperature in borate buffer in the presence of the Ni(II) macrocyclic complex (118) resulted in phenol containing the ^{17}O isotope in the OH group. ESR spectra proved the formation of an O_2 adduct with strong superoxide character. No isotope effect was observed with C_6D_6 and therefore (119) was proposed as an intermediate of hydroxylation [329].



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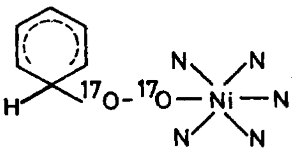

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The mixed metal acetate complex $K_2Pd(OAc)_4$ has been found to catalyze the benzylic acyloxylation of toluene with O_2 in a carboxylic acid as solvent at 165-170°C:

$$PhCH_3 + RCOOH \xrightarrow{O_2} PhCH_2OOCR$$

Minor byproducts were benzaldehyde, benzoic acid and CO_2 [330].

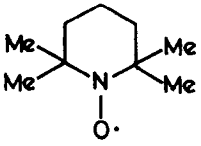
Oxidation of cumene in liquid phase by O_2 in the presence of Cu(I) and Cu(II) pyridine or triphenylphosphine complexes was studied. The Cu(I) compounds act as both catalysts and inhibitors [331].

2. Catalytic oxidation of O-containing Functional Groups with O_2

a) Oxidation of Alcohols

The stoichiometric reaction of a dodecamolybdo-heteropolyanion /HPA/ in the oxidation of cyclohexanol to cyclohexanone and adipic acid turns to catalytic in the presence of H_2O_2 or with aeration of the reaction mixture in the presence of charcoal. H_2O_2 and O_2 act by reoxidizing HPA reduced in the reaction with the substrate [332]. The oxidation of 2-ethylhexanol in the presence of Co 2-ethylhexanoate at 90°C gives 2-ethylhexanoic acid with up to 90% selectivity [333].

Methylcyclohexanols can be dehydrogenated with Rh-phosphine catalysts and O_2 at 85°C. The dehydrogenation proceeds faster in the case of the less stable cis isomers [334]. Cyclohexanol was oxidized to cyclohexanone by O_2 in the presence of $RhCl_3.3H_2O$ under acidic conditions. The addition of $FeCl_3$ promoted the catalytic conversion. Water was formed in equimolar amounts and under optimum conditions 40-45% yield of ketone could be achieved [335]. Secondary alcohols RR′CHOH [R = Me; R′ = Bu, hexyl, octyl; RR′ = $(CH_2)_5$] were oxidized at 70°C and 1 bar of O_2 to give RCOR′ with high selectivity using catalyst systems containing $RhCl_3$ or $[Rh(H_2O)_6]X_3$ ($X = BF_4$, ClO_4) and $BiCl_3$ and LiCl [336]. A homonuclear Cu(II)-Cu(I) complex has been prepared from a homobinuclear di-μ-hydroxo-bridged Cu(II) complex and tetramethyl-p-phenylenediamine. The new mixed-valence complex acted as catalyst in the oxidation of alcohols with O_2 to aldehydes [337]. The room temperature oxidation of allylic and benzylic alcohols by O_2 using a catalyst mixture of CuCl and nitroxyl (120) was reported. A more general oxidation of primary alcohols was realized by $CuCl_2$ mediated by (120). Under these latter conditions a base is necessary to take up the HCl that is generated [338].



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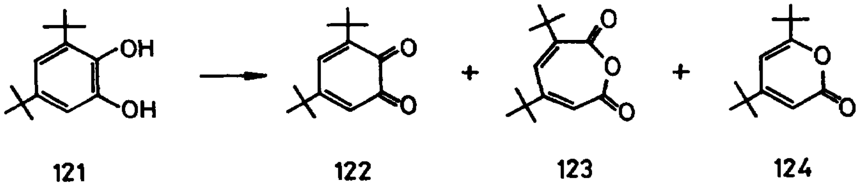
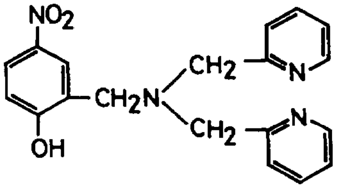
See also [360, 532].

b) Oxidation of Phenols

Several catecholato complexes of vanadium containing a Schiff base as ligand were prepared and tested as catalysts for the oxygenation of catechols [339]. Binuclear vanadyl(IV) complexes like $VO(acac)(OMe)_2$ catalyze the oxidation of 3,5-di-tBu-catechol (121) to 3,5-di-tBu-o-quinone (122), 2,4-di-tBu-muconic anhydride (123) and 4,6-di-tBu-2H-pyrane-2-one (124) by O_2.



The main product of the reaction is (123) indicating that these V complexes act in a manner similar to pyrocatechase. In the case of unsubstituted catechol or o-phenylenediamine as substrates the corresponding cleavage product could not be detected [340]. The Fe(III)-nitrilotriacetate complex catalyzes the oxidative cleavage of catechols. Reacting salts of the (nitrilotriacetato) (3,5-di-tert-butylcatecholato)ferrate(III) dianion with $^{18}O_2$, cleanly a single ^{18}O atom is incorporated into the product [341]. The iron(III) complex $Fe(bpnp)Cl_2$ (Hbpnp = 125) catalyzes the oxidative cleavage of catechol (121) by O_2 in nitromethane to give the corresponding muconic acid anhydride (123). The visible spectrum of the complex shows changes during oxidation which are similar to those observed with the enzyme pyrocatechase [342].



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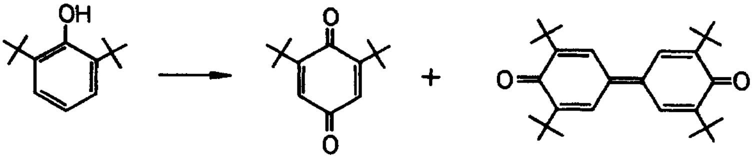
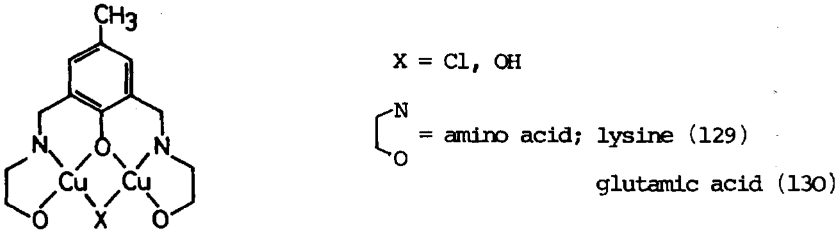
Several Co(II) complexes like $Co(acac)_2$ and Co(salen) catalyze the oxidation of guaiacol by air in basic water solutions [343]. Homonuclear Cu(II), Pd(II), Zn and Co(II) and heterodinuclear Pd-Ni and Pd-Cu complexes of methylmethionine were prepared and used as catalysts for the oxidation of (121) to (122)[344]. The rates of oxidation of (126) by O_2 in DMF have been investigated with Co(TPP), Fe(TPP)Cl, Mn(TPP)Cl and VO(TPP) as catalysts. The activities of the catalysts decreased in the stated order. The order of selectivity for the formation of (127) relative to (128) was Co(TPP) $\gg$ VO(TPP) > Fe(TPP)Cl > Mn(TPP)Cl. The results were interpreted with a mechanism in which an intermediate dioxygen complex is required for the formation of (127) but not for that of (128) [345].



126 127 128

The dicopper(II) complexes 129 and 130 were anchored to polystyrene and oxirane acrylic beads and used as catalysts for the oxidation of catechol (131). The activity of these supported complexes was less than that of their homogeneous analogues [346].



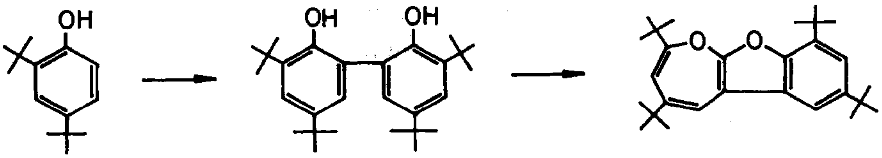
X = Cl, OH

= amino acid; lysine (129)

glutamic acid (130)

131

Autoxidation of phenols with O_2 catalyzed by Cu(II)-ethylenediamine complexes was investigated. Primary products were 2,2'-biphenyldiols (132). Depending on the bulkiness of the substituents the secondary products were either a benzofuran (133) or a dioxepin (134) [347].



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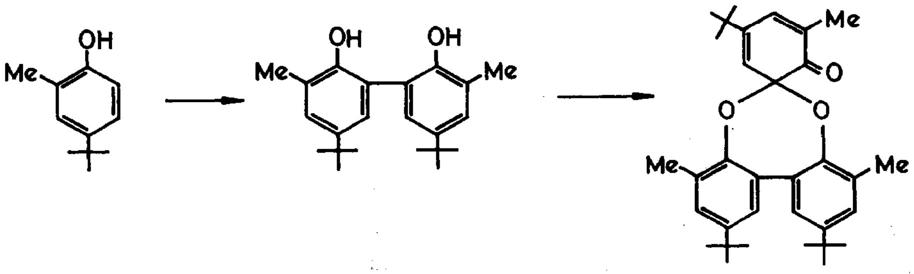

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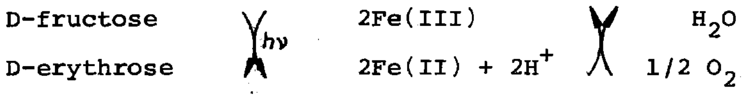
134

c) Oxidation of Aldehydes and Ketones

On the basis of earlier experimental data obtained in the oxidation of sulfite and benzaldehyde by dioxygen with transition metal ions as catalysts an oxidation mechanism involving catalytic and photocatalytic effects was proposed [348].

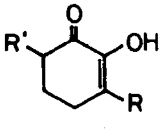
The kinetics of the complete oxidation of benzaldehyde in the presence of iron and cobalt salts was investigated [349]. D-Fructose was oxidatively degraded to D-erythrose by atmospheric oxygen with irradiation in the presence of $FeCl_3$. The reaction proceeded by coupling with the oxidation-reduction cycle of iron ions as shown schematically below:



D-Glucose + $FeCl_3$ and D-fructose + $MnCl_2$ systems were also found to be susceptible to catalytic photooxidation [350].

Chemical oscillations in autoxidation of MeCHO and PhCHO in the presence of $Co(OAc)_2$ and NaBr involve a radical mechanism. The oscillation is quenched by hydroquinone [351]. Ketones were oxidized to α -diketones and carboxylic acids at 20-60°C by O_2 in aqueous-alkaline solutions of Co-phen complexes. A kinetic study indicated that an O_2-enol-Co-phen complex is formed [352]. The liquid-phase oxidation of several aldehydes to carboxylic acids with O_2 catalyzed by Co(II) salts has been studied. The main side reaction was the decarbonylation of acyl radicals leading to the formation of hydrocarbons or alcohols with a one-carbon atom shorter chain than the starting aldehyde. Ketones, α-diketones and esters were also detected among the products [353]. The kinetics of the co-oxidation of benzaldehyde and propene by O_2 to give perbenzoic acid and propene oxide was studied in the presence of Co(*p*-MeTPP), $Co(OAc)_2.4H_2O$ and $Co(NAP)_2$ as catalysts (NAP = 2-nitraminopyridine). A long induction period was observed with the porphyrin complex which was absent with the other catalysts [354]. The kinetics of the oxidation of benzoin to benzil by O_2 catalyzed by Ni acetate or Co acetate in methanol and ethanol have been determined. The overall reaction was second order in benzoin. Significant amounts of benzaldehyde and benzoic acid were formed as byproducts in reactions that are independent from benzil formation [355].

1,2-Cyclohexanediones (135) are dioxygenated by O_2 with Cu^{2+} as catalyst to afford 1,5-keto acids (136) and CO. Methyl α-hydroxyadipates (137) are also formed as byproducts [356].



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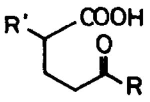

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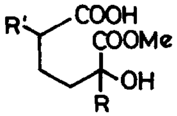
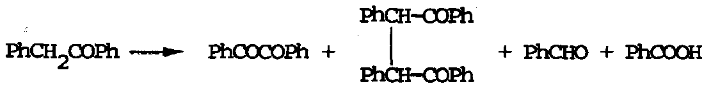


137

Deoxybenzoin (138) is converted by a Cu(II) + py + Et_3N + MeOH + O_2 system to benzil (139), bidesyl (140), PhCHO and PhCOOH. Formation of (140) needs only Cu(II), that of (139) and PhCHO both Cu(II) and O_2. Benzoic acid is formed from (139) by Cu(II) and water [357].



$$PhCH_2COPh \longrightarrow PhCOCOPh + \begin{array}{c} PhCH{-}COPh \\ | \\ PhCH{-}COPh \end{array} + PhCHO + PhCOOH$$

138 139 140

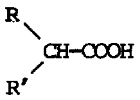
d) Miscellaneous Oxidations

Liquid-phase oxidation of dibenzyl ether catalyzed by 3d metal acetylacetonates $M(acac)_n.xH_2O$ ($n = x = 2$, $n = 3$, $x = 0$; $M = VO^{2+}$, Cr^{3+}, Mn^{2+}, Mn^{3+}, Fe^{3+}, Co^{2+}, Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) yields PhCHO, PhCOOH, or $PhCH_2OCH(OOH)Ph$ [358].

The oxidation of dihydroxyfumaric acid by O_2 is first order in substrate, in Fe^{2+} catalyst, and O_2 [359]. Cobalt phthalocyanine adsorbed on SiO_2 gel was used as catalyst for the oxidation of oxalic acid and the dehydrogenation of iPrOH [360]. $Co(acac)_2$ acts as an initiator for the thermal oxidation of diethyl maleate as well as of butyl- and methylmethacrylate and catalyzes the decomposition of the oxidation products, leading to additional initiation [361].

EDTA acts as an inhibitor of vitamin C oxidation in aqueous solutions containing Ag^+ and Pd^{2+} as well as alkali ions [362]. Autoxidation of L-ascorbate is catalyzed by Cu(II)-poly(L-histidine). The binding between Cu(II) and poly(L-histidine) is rather labile at pH 4.0 and this labile Cu(II) is assumed to be catalytically active [363]. The oxidation of ascorbic acid in the presence of a tetrabenzotetraaza macrocyclic complex of copper was investigated [364].

Carboxylic acids of type (141) or (142) are oxidatively decarboxylated into ketones (143) by O_2 in the presence of copper(I) in MeCN as solvent:



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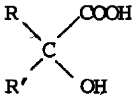

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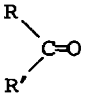


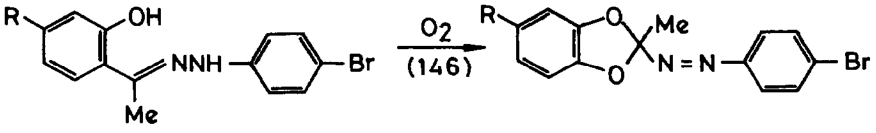
143

Probably Cu(III) carboxylates are the intermediates [365].

3. Catalytic Oxidation of N-containing Organic Compounds with O_2

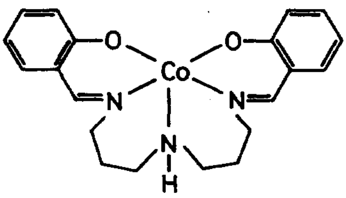
Autoxidation of dimethylformamide is catalyzed by phen complexes of Fe(II), Fe(III), Co(II), Co(III) and Cu(II). Carbon dioxide and dimethylamine are the products [366]. The oxidation of (−)-DOPA by optically active Co(III) complexes like $[CoCl(NH_3)$

(ethylenediamine)$_2$]Br$_2$ has been studied. Optical rotation measurements proved the formation of an intermediate Co complex containing DOPA or its oxidation product [367]. Substituted 2'-hydroxyacetophenone phenylhydrazones (144) are readily oxygenated in the presence of Co(salpr) (146) in ethanol at room temperature to give 1,3-benzodioxoles (145) in good yield [368].



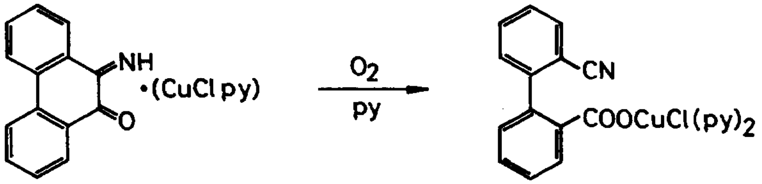
144

145, R=H, Me, MeO, Cl, NO$_2$



146

Dihydrazones of α-diketones, H$_2$NN=CRCR=NNH$_2$ (R = Ph, pentyl) were oxidized stoichiometrically by the CuCl$_2$-O$_2$-py complex in CH$_2$Cl$_2$ at room temperature to give disubstituted acetylenes RC≡CR, in good yield. Oxidation also proceeded with catalytic amounts of CuCl$_2$ under O$_2$ [369]. Copper(I) chloride adducts of the monoimines of 9,10-phenanthrenequinones (147) are transformed by O$_2$ into the carboxylato Cu(II) complexes (148). This stoichiometric reaction models the copper-catalyzed oxidation of o-quinones into semi-nitriles of muconic acids in the presence of ammonia [370].



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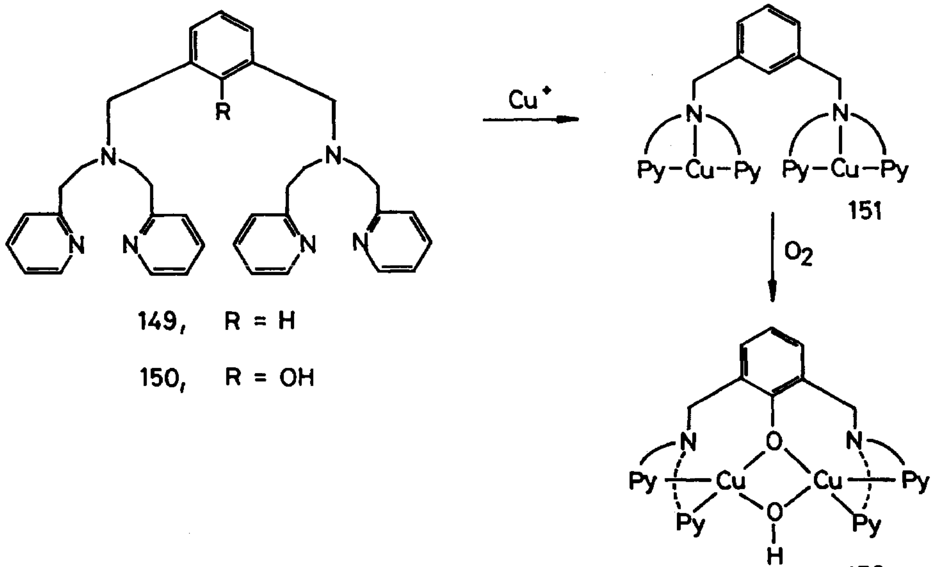
148

The oxidation of dimedone bisguanylhydrazone by air is catalyzed by Cu(II) and the catalytic effect increases in the presence of py. The reaction has analytical significance [371]. The dinuclear 3-coordinate Cu(I) complex (151) reacts with O_2, and specific hydroxylation of the aromatic ring occurs in > 90% yield which produces the binuclear pentacoordinate complex (152). Measurements using $^{18}O_2$ show that the phenolate and hydroxy oxygen atoms in (152) are derived from dioxygen. Removal of the Cu ions from (152) gives the phenol (150) completing the sequence of the copper-mediated hydroxylation of the aromatic ring (149) ⟶ (150) [372].



149, R = H

150, R = OH

151

152

Dehydrogenation of 5-trifluoromethyldihydrouracil (153) and its substituted derivatives could be performed with stoichiometric amounts of $CuBr_2$ at 115°C in DMF/AcOH. Good to excellent yields of the corresponding uracil derivatives (154) were obtained. In an O_2 atmosphere also catalytic amounts of $CuBr_2$ were sufficient but the reaction time was significantly longer [373].

153

154

4. Catalytic Oxidation of P-, S-, or Halogen-containing Organic Compounds with O_2

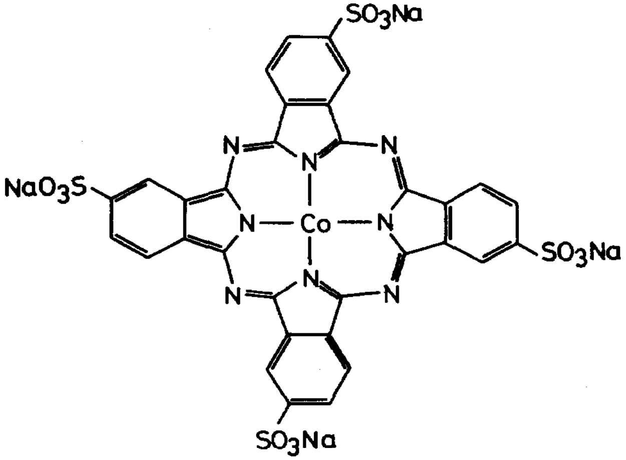
PPh_3 was oxidized by O_2 to $OPPh_3$ in MeCN using FeX_3 and $FeX_3(OPPh_3)_2$ (X = Cl, Br, -NCS) as catalyst. The rate of oxidation increased in the order Cl < -NCS < Br [374]. CpRu(L), [L = η^5-pentakis(methoxycarbonyl)cyclopentadienyl] catalyzes the oxidation of Ph_3P by O_2 in nitrile solvents. The ligand L is replaced by phosphine in the course of this reaction [375]. The complexes $Ru(OEP)(PPh_3)_n$ (n = 1,2) react in toluene with O_2 to generate $OPPh_3$, RuO_2 and the parent porphyrin $H_2(OEP)$. This reaction is initiated by the coordination of O_2 to $Ru(OEP)(PPh_3)$. In contrast, the catalytic oxidation of excess PPh_3 with O_2 in the presence of $Ru(OEP)(PPh_3)_2$ probably goes via an initial outer-sphere reaction that generates O_2^- and Ru(III). The PPh_3 is oxidized by H_2O_2 formed from the superoxide [376]. The o-phenylenediamine/Co(II) system catalyzes the oxidation of Ph_3P to Ph_3PO by O_2. Both O atoms of O_2 are utilized in this oxidation. A complex with the composition $[Ph_3P(OPD)_2Co\text{-}O\text{-}O\text{-}Co(OPD)_2PPh_3]^{4+}$ (OPD = o-phenylenediamine) was characterized as an intermediate [377]. The co-oxygenation of cyclooctene and PPh_3 with O_2 and $Rh_2(cyclo\text{-}octene)_4Cl_2$ as catalyst yields the allylic alcohol cyclooct-2-ene-1-ol and Ph_3PO. Experiments with D-labeled substrate show that oxygen attacks at the vinylic hydrogen and this is followed by double bond migration [378].

Complexes of Cu(II), Mn(II), Mn(III) and Co(II) with acac or salicylaldehyde imine ligands catalyze chain termination in Me_2SO oxidation with O_2 [379]. The oxidation of dialkyl sulfides by O_2 can be effectively catalyzed by cis- or trans-$RuX_2(Me_2SO)_4$ complexes (X = Cl, Br). The reaction takes place only in alcohols as solvents and for every mole of sulfide 1 mole of alcohol is oxidized to the corresponding carbonyl compound. According to kinetic and ^{18}O-labeling studies, Ru(II) is oxidized by O_2 to Ru(IV) and peroxide, the sulfide is oxidized by peroxide, and Ru(IV) is reduced by alcohol [380]. Rate constants were determined for the oxidation of R_2NCS_2Na (R = Et, R_2N = piperidino) with O_2 and different macroheterocyclic complexes of Co [381]. Cobalt phthalocyanine and di-Na cobalt disulfophthalocyanine catalyze the removal of thiols from hydrocarbons by oxidation [382]. A kinetic study has been performed of the oxidation of 2-mercaptoethanol by O_2 using Co(II) phthalocyanine tetrasodium sulfonate (155) attached to poly(vinylamine) as a catalyst. The stoichiometry of the reaction is the following:

$$2\ HOCH_2CH_2SH + O_2 \longrightarrow HOCH_2CH_2SSCH_2CH_2OH + H_2O_2$$

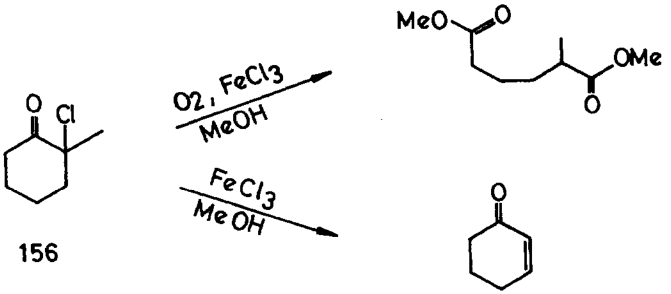
$$2\ HOCH_2CH_2SH + H_2O_2 \longrightarrow HOCH_2CH_2SSCH_2CH_2OH + 2\ H_2O$$

The polymeric catalyst exhibits large activity and an enzyme-like behavior (Michaelis-Menten kinetics). Radicals are reaction intermediates [383].



155

Continuous flow epoxidation of allyl chloride by air in the presence of $V(acac)_3$ catalyst dissolved in dimethyl phthalate, carried out at 150-170°C gave epichlorohydrin in low yields with 96% selectivity [384]. Oxidation of a mixture of allylchloride and ethylbenzene in the presence of graphite lamellar compounds containing $MoCl_2$ or $MnCl_2$ yields epichlorohydrin. The olefin is epoxidized by the α-phenyl ethyl hydroperoxide formed [385]. Oxidation of p-chlorotoluene by air catalyzed by hemin-thiol complexes yields hydroxylation products (chloro-methyl-phenols), *p*-chloro-benzyl alcohol and *p*-chloro-benzaldehyde [386]. 2-Halo-cyclohexanones like (156) are oxidized by air and $FeCl_3$ as catalyst in methanol solution into adipic acid dimethyl esters (157). In the absence of oxygen only dehydrochlorination occurs yielding (158) [387].



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158

5. Catalytic Oxidation of Organic Compounds with Organic or Inorganic Oxidants

a) Oxidation of Hydrocarbons or Hydrocarbon Groups

The complex $CrO_5.Ph_3PO$ oxidizes hydrocarbons in the presence of tBuOOH to alcohols and ketones. The oxidation is partly catalytic [388]. The cyclohexenones (159) are oxidized by $K_2Cr_2O_7$ and air in the presence of phosphomolybdic acid and $CuSO_4.5H_2O$ to the cyclohexenediones (160) in 60% yield [389].

R = H, Me

159

160

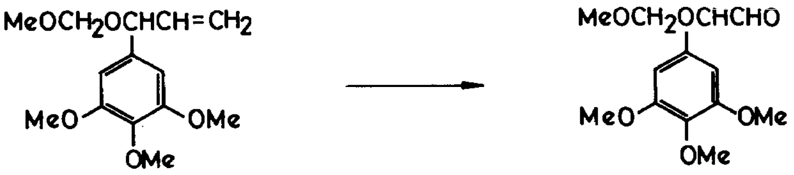
Oxidation of olefins with tBuOOH in the presence of $Cr(CO)_6$ or $Cr(CO)_3(MeCN)_3$ produces enones by allylic methylene oxidation. The catalyst may be recovered almost quantitatively. In certain cases this oxidation proceeds selectively even in the presence of a secondary alcohol, cf. oxidation of (161) [390].

60 %

161

cis-Stilbene, styrene, cyclohexene, and norbornene were oxidized with Mn(III)-bleomycin and PhIO or O_2 (in the presence of ascorbate). Epoxides and ketones were the main products and the results were quite similar to those obtained for metalloporphyrins [391].

Aliphatic ketones are converted into γ- and δ-diketones on oxidation with $Na_2S_2O_8$ in the presence of $FeSO_4.7H_2O$ in water solution at 80°C. Yields are around 50% [392]. Mono- and disubstituted alkenes were transformed into *trans*-vicinal diacetates by an Fe^{2+}/persulfate/AcOH system. A mechanism was proposed [393]. Meso-tetra(2,6-dichlorophenyl)porphinatoiron(III) chloride was found to be an unusually efficient catalyst for alkene hydroxylation and epoxidation by pentafluoroiodosyl benzene as oxidizing agent. Turnover numbers up to 10000 were achieved. The high activity of the catalyst is attributed to its resistance against μ-oxo dimer formation and oxidative destruction [394]. Oxidation of 3,3,6,6-d_4-cyclohexene, methylenecyclohexane, and β-pinene has been examined with cytochrome P-450, Fe(TPP)Cl + PhIO and Cr(TPP)Cl + PhIO. Epoxidation and allylic hydroxylation were the primary reactions. Allylic hydroxylation was accompanied by extensive rearrangement in most cases. A mechanism was suggested involving initial H atom abstraction from the allylic site [395]. Rate constants for Os(VIII)-catalyzed oxidation of maleic, fumaric, acrylic, and cinnamic acids by vanadium(V) were determined [396]. The allylic double bond in (162) was oxidatively cleaved with KIO_4 in the presence of dibenzo-18-crown-6 ether and OsO_4 to yield the aldehyde (163) [397].



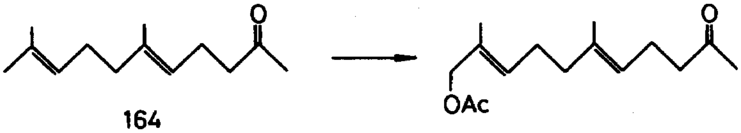
162

163

Oxidation of cyclohexene by cumene hydroperoxide is catalyzed by cobalt tetra-4-*tert*-butylphthalocyanine. The reaction involves radicals formed by decomposition of the peroxide [398].

Chlororhodium(III) complexes catalyze the oxidation of 1-octene by tBuOOH in alcoholic solvents to yield mainly octanone-2 [399].

Olefins are converted into allylic acetates by treatment in acetic acid with a catalytic amount of $Pd(OOCCF_3)_2$ and one equivalent of benzoquinone as oxidant. The reaction is selective for oxidation of a terminal methyl group of geranylacetone (164) [400].



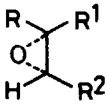
164

β -Aryl carbonyl compounds are the major products in the oxidation of styrenes by $S_2O_8^{2-}$ + Cu(II). Initially, radical cations are formed which add water to give β -hydroxylalkyl radicals followed by Cu(II) oxidation to epoxide. Acid catalyzed rearrangement yields the product [401].

See also [469].

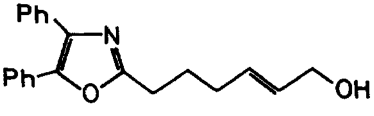
b) Epoxidation of Olefins

Epoxidation of (Z)- and (E)-$Me(CH_2)_5CH{=}CHCH_2OH$ with tBuOOH in the presence of $Ti(OPr^i)_4$ and D-tartaric acid dimethyl ester gave the epoxides (165a; R, R^1, R^2 = H, hexyl, CH_2OH) and (165b; R, R^1, R^2 = hexyl, H, CH_2OH), respectively. The enantiomeric excess of (165b) was greater than that of (165a) [402].



165

Based on kinetic data and enantioselectivity the mechanism of the Ti tartrate-catalyzed asymmetric epoxidation of olefins with t-BuOOH was discussed. The alignment of a lone pair of the reactive alkyl peroxo O atom with the olefin π^* orbital was postulated as an important interaction in the transition state [403]. Allylic alcohols containing a 4,5-diphenyloxazole group (166) were asymmetrically epoxidized using the Sharpless method. The oxazole group may be easily transformed into an ester group. Since epoxidation of allylic esters is not possible directly, this method enables the synthesis of chiral ester epoxides (167) [404].



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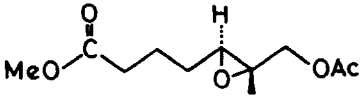

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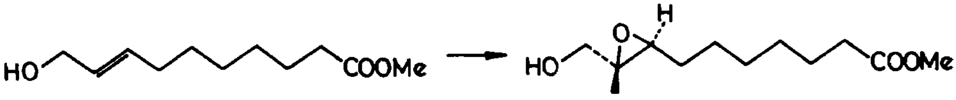
The allylic alcohol (168) was epoxidized with tBuOOH in the presence of L(+)-diethyl tartrate and $Ti(OPr^i)_4$ to the 8S,9S-epoxy alcohol (169) with 69% yield.



168 169

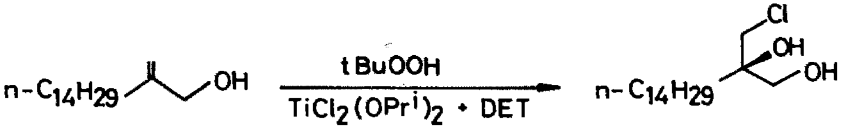
The alcohol (169) was further oxidized into the corresponding aldehyde with CrO_3/py in dichloromethane [405]. Kinetic resolution of (±)-(170) was carried out at -50°C by epoxidizing with the Sharpless-system [tBuOOH + $Ti(OPr^i)_4$ + (+)-diisopropyltartrate to give (171) and unreacted (+)-(170b) [406].

170a R=OH; R'=H

170b R= H; R'=OH

171

Chiral tartrate esters linked to 1% crosslinked polystyrene resins via $-CH_2OH$ or $-CH_2CH_2OH$ groups were used in the epoxidation of geraniol with tBuOOH and $Ti(OPr^i)_4$ catalyst. 2S,3S-Epoxygeraniol was obtained with up to 66% enantiomeric excess [407]. The Sharpless reagent for asymmetric epoxidation was modified by addition of 1 mol equiv. of water to give a new homogeneous reagent [$Ti(OPr^i)_4$/ /diethyltartrate /H_2O/tBuOOH = 1:2:1:1]. This reagent cleanly oxidizes prochiral sulfides into optically active sulfoxides with 50-90% optical yield [408]. Use of $TiCl_2(OPr^i)_2$ instead of $Ti(OPr^i)_4$ with (+)-diethyltartrate (DET) (in a 2:1 ratio) affords the chloro diols (172) arising from regiospecific opening of intermediate epoxides of opposite enantioselectivity to those produced in the analogous standard asymmetric epoxidation:



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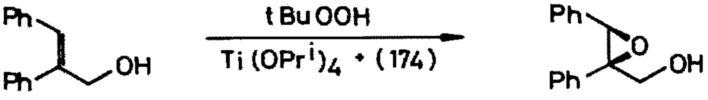
Similar "inverse" epoxides (173) are also obtained in oxidations catalyzed by $Ti(OPr^i)_4$ and tartramide ligands [for example (174)] in the 2:1 ratio [409].



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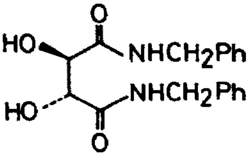
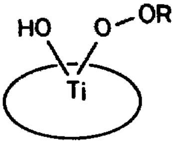


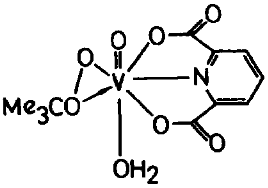
174

Asymmetric epoxidation of homoallylic alcohols using the $Ti(OPr^i)_4$, (+)- or (-)-diethyl tartrate, and tBuOOH system affords products with 23-55% optical yields. The enantiofacial selection is opposite to that observed for allylic alcohols [410]. The well--characterized oxotitanium complex (TPP)Ti=O is a catalyst for the epoxidation of cyclohexene with tBuOOH at 70°C. The cis-hydroxo alkylperoxo complex (175) is proposed to be involved in the catalytic cycle [411].



175

Epoxidation of vitamin D_3 with tBuOOH catalyzed by $VO(acac)_2$ in benzene afforded (5S)-5,6-epoxyvitamin D_3 in 90% yield. The same epoxidation with $Mo(CO)_6$ as catalyst resulted in a mixture of three epoxides and the reaction needed reflux temperature [412]. The oxidation of hydrocarbons by H_2O_2 and ROOH catalyzed with d^o metal peroxides, e.g. (176), involves heterolytic or homolytic cleavage of the triangular peroxide moiety. The mechanism of selective heterolytic epoxidation comprises the peroxymetalation of the coordinated olefin. Homolytic epoxidations are less selective [413].



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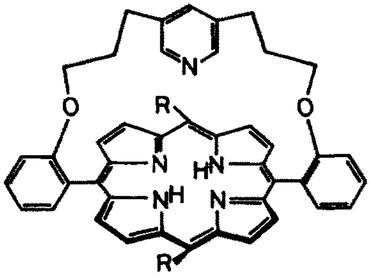
Cyclohexene was epoxidized with tBuOOH in the presence of Mo(V)-TPP complexes with up to 84% selectivity. In the epoxidation of alkenes (hexene, isoprene) higher rates of cis vs. trans isomer was obtained with Mo(TPP)(=O)X than with $Mo(CO)_6$ due to the steric control of the macrocyclic ligand [414]. The catalytic activity of molybdenum oxalate, EDTA,and phenoxy complexes in epoxidations carried out with tBuOOH varied with the ligand used. The complex containing phenoxy ligands was the most active in the reaction investigated [415]. Epoxidation of allylic alcohols with H_2O_2 is catalyzed by cetylpyridinium 12-molybdatophosphate. The epoxidation of geraniol proceeds with high regio- and stereoselectivity [416]. Epoxidation of sardine oil by cumene hydroperoxide in the presence of Mo acetylacetonate as catalyst is best performed at 116°C [417]. Epoxidation of olefins with cumyl hydroperoxide was studied. Best conversions and selectivities were obtained with Mo_2B_5 combined with Co or Mn stearate [418]. The decomposition of hydroperoxides like tBuOOH or $PhCMe_2OOH$ by $MoO_2(acac)_2$ and similar Mo(VI) complexes is a molecular and not a free radical mechanism. The significance of this decomposition reaction in the Mo-catalyzed epoxidation of olefins was discussed [419]. Kinetics and selectivity of epoxidation of cyclopentene, cyclohexene, cyclooctene, 2-methyl-2-butene and of styrene with hydroperoxide in the presence of MoO_2^{2+} and VO^{2+} immobilized on a chloromethylated copolymer of styrene + divinylbenzene were determined [420].

Di-, tri- and tetrasubstituted olefins may be epoxidized with high yields using NaOCl as oxygen source and Mn(TPP)OAc as catalyst in the presence of pyridine. Epoxidation is stereospecific with *syn* addition of the oxygen atom [421]. The catalytic epoxidation of terminal olefins with NaOCl and Mn(TPP)OAc is not possible with reasonable yields because the oxidative decomposition of the catalyst competes with the epoxidation of the poorly reactive olefin. It has now been found that using modified porphyrine ligands containing substituted Ph groups like C_6F_5 or *o*-F-C_6H_4, 20-80% yields of epoxides may be obtained [422]. The effect of various substituted pyridines on the stereoselectivity of epoxidation of *cis*-stilbene with the NaOCl/Mn(TPP)OAc system has been investigated. The stereoselectivity increased with ligands which strongly coordinate to the metal. This was attributed to the formation of $Mn(TPP)(=O)L^+Cl^-$ complexes (L = substituted py) with a more oxenoid character of the Mn=O group ensuring a more concerted transfer of oxygen [423]. The effect of pyridine on the stereoselectivity of olefin epoxidation by NaOCl catalyzed by Mn(III)-porphyrin complexes was discussed [424]. Kinetic data suggest that the rate determining step in the epoxidation of cyclohexene by Mn(TPP)OAc and NaOCl is the conversion of a Mn(III)-species into an oxo-manganese (V)-species (TPP)Mn=O. Anchoring of the porphyrin to a support increases the rate of epoxidation by preventing the formation of inactive dimers [425]. Epoxidation of *cis*-stilbene by NaOCl was catalyzed by Mn(TPP)OAc and the Mn(porphin)Cl complexes containing the porphin ligands (177) or (178). In the case of Mn(TPP)OAc addition of pyridine significantly changed the *cis*:*trans* epoxide ratio but no such effect was noted with the catalysts containing ligands (177) or (178). This proves that pyridine acts as the fifth (axial) ligand in the TPP-systems [426].



R + R = $-C_6H_4O(CH_2)_{12}OC_6H_4-$ 177

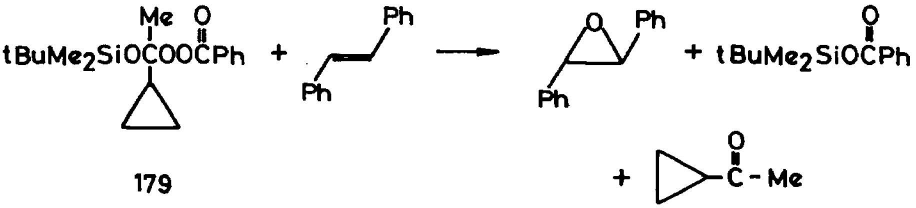
$-C_6H_4O(CH_2)_4C_6H_4(CH_2)_4OC_6H_4-$ 178

In the presence of imidazole, Mn(TPP)Cl and Fe(TPP)Cl catalyze the decomposition of cumyl hydroperoxyde. Transiently probably a high-valent oxo complex is formed. If olefins are present, epoxidation takes place [427]. p-Cyano-N,N-dimethylaniline N-oxide epoxidizes cyclohexene in the presence of Mn(TPP)X (X = halide, OCN^-). The Mn complexes accept the O of the N-oxide as "oxene" to generate O=Mn(TPP)(X) which reacts with cyclohexene to yield the epoxide. The rate constants for this oxene transfer depend upon the ligand X, the rate of O transfer to cyclohexene is very large [428]. The rate-determining step in the Mn(III) porphyrin-catalyzed epoxidation of olefins by LiOCl is the decomposition of a relatively stable intermediate formed from the olefin and a high-valent Mn-oxo complex to Mn(III) porphyrin and epoxide [429]. Soluble metal ion salts of Mn, Fe, Co and Cu catalyze epoxidation and hydroxylation of olefins and of cumene by iodosylbenzene in MeCN. The catalytic properties of the Fe and Mn salts with regard to stilbene epoxidation are remarkably similar to those of the Fe and Mn porphyrins [430].

Technetium compounds were used as catalysts for the epoxidation of cyclohexene with tBuOOH. Highest yield (32%) was achieved with $Tc_2(CO)_{10}$ [431].

Oxidation of styrene and stilbene by PhIO was studied in the presence of $FeCl_3$, $Fe(acac)_3$ and Fe(TPP)Cl. Epoxidation is the main reaction with all three catalysts. If O_2 is present, autoxidation to benzaldehyde becomes the predominant reaction with $FeCl_3$ and $Fe(acac)_3$ [432]. Epoxidation of olefins by $NaIO_4$ was effected with $RuCl_3.nH_2O$ as catalyst in the presence of bpy. The method is especially suited for internal olefins. It is *syn* and stereospecific for both E and Z alkenes and no isomerization occurs [433].

The cyclopropyl-substituted silyloxyalkyl peroxybenzoate (179) transforms olefins into epoxides in the presence of a catalytic amount of $Pd(OAc)_2$. Electron-deficient olefins are inert under the conditions. *Trans* olefins yield exclusively *trans* epoxides, from *cis* olefins *cis* epoxides are the main products [434].



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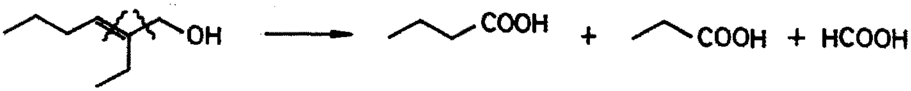
The complex (dppe)Pt(CF_3)(OH) catalyzes the epoxidation of terminal alkenes with 35% H_2O_2. Water is an essential requirement of the system. The selectivity of the reaction is over 99% [435].

Olefins can be epoxidized by iodosylbenzene in the presence of Cu^{2+} ions in acetonitrile as solvent. If Cu^+ ions are used, the yields are much lower and an induction period is observed. Both stilbene isomers give trans-stilbene oxide [436].

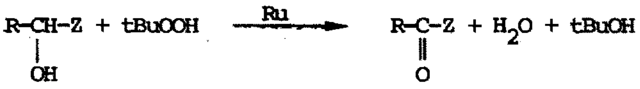
See also [385, 394, 395, 401, 475].

c) Oxidation of O-containing Functional Groups

$ZrO(OAc)_2$ catalyzes the selective oxidation of primary alcohols with tBuOOH into aldehydes with very good yields without formation of carboxylic acids. Allylic alcohols are converted into α, β-unsaturated aldehydes [437]. Chromium(III) supported on Nafion 511 was used to catalyze the oxidation of alcohols to the corresponding carbonyl compounds with tBuOOH. The recovered catalyst could be reused without loss of the Cr(III) ion [438]. Benzyltrimethylammonium tetrabromooxomolybdate is a selective catalyst for the oxidation of secondary alcohols to ketones, primary alcohols to esters, and aldehydes to acids or esters with tBuOOH. Olefinic double bonds are not affected [439]. In the presence of $(NH_4)_6Mo_7O_{24}.4H_2O$ and K_2CO_3, hydrogen peroxide oxidizes secondary alcohols to ketones and primary alcohols to carboxylic acids. The oxidations are chemoselective, olefins are not transformed into epoxides. The alcohol oxidation in preference to olefin epoxidation stems from the presence of potassium carbonate [440]. Allylic alcohols are oxidized with excess tBuOOH in the presence of Mo complexes like $MoO_2(acac)_2$ to carboxylic acids with shorter carbon chains. The molecule is cleaved regioselectively at the double bond and at the single bond between the olefinic and the allylic carbon atoms [441]:



The oxidation of mandelic acid by Fe(II) + H_2O_2 (Fenton's reagent) produces benzaldehyde and phenylglyoxylic acid. Product distribution studies suggest an Fe(IV) species as intermediate [442]. Oxidation of dihydroxyfumaric acid by H_2O_2 in the presence of Fe^{2+} as catalyst is first order in Fe^{2+}, substrate and oxidant [443]. The Fe complex of the tetramethyl ester of coproporphyrin III adsorbed at an octane/water interface catalyzes the oxidation of ascorbate (dissolved in the water phase) by 2-N-methylamino-1,4--naphthoquinone dissolved in the organic phase [444]. The kinetics of Ru(III)-catalyzed oxidation of lactic acid and acrylic acid by alkaline hexacyanoferrate(III) has been examined. The rate determining step is the displacement of OH^- from $Ru(H_2O)_{6-x}(OH)_x^{(3-x)+}$ by the substrate and this is followed by hydride abstraction from the substrate [445]. Kinetics and mechanism of the Ru(III)- and Ir(III)-catalyzed oxidation of iPrOH by phenyl iodosoacetate were determined [446]. The Ru(III)-catalyzed oxidation of aryl styryl ketones by periodate in acid medium to the corresponding substituted benzoic and phenylacetic acids is first order each in IO_4^- and Ru(III) and fractional order in substrate [447]. The Ru(III)--catalyzed oxidation of 1,3-butanediol by phenyl iodosoacetate to 3-hydroxybutanal is first order with respect to oxidant and zero order with respect to substrate [448]. The $RuCl_3$-catalyzed oxidation of cyclopentanol, cyclohexanol and cycloheptanol by Ce(IV) sulfate in aqueous sulfuric acid was investigated. A Ru(III) hydride was proposed as an intermediate [449]. Rate constants for the oxidation of cycloalkanols to the corresponding ketones by $Fe(CN)_6^{3+}$ in mild alkalic, aqueous medium were determined in the presence of traces of Ru(VI). The oxidation proceeds via the formation of a complex between Ru(VI) and the substrate [450]. Based on kinetic experiments a mechanism has been suggested for the oxidation of diols by alkaline hexacyanoferrate(III) catalyzed by RuO_4. A Ru(VIII) hydride species is supposed as an intermediate [451]. Dehydrogenation of α-hydroxyesters and α-hydroxynitriles by tBuOOH is catalyzed by a large number of Ru(O)-, Ru(II)-, and Ru(III)-compounds. Even Ru on carbon is a useful catalyst [452]:

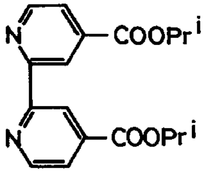


$$\underset{\displaystyle OH}{R\text{-}\underset{|}{C}H\text{-}Z} + tBuOOH \xrightarrow{Ru} R\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}Z + H_2O + tBuOH$$

R = Me, Ph, 2-furyl, 2-thienyl, (E)- PhCH=CH

Z = COOMe, COOEt, CN

The Ru(II) polypyridyl complex RuL_3^{2+} (L = 180) catalyzes the photo-oxidation of benzylic alcohols to aldehydes by visible light in the presence of a diazonium salt (181) as quencher and a base. The diazonium salt is concomitantly reduced to benzophenone and fluorenone [453].



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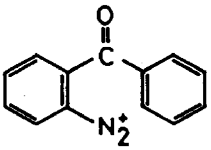
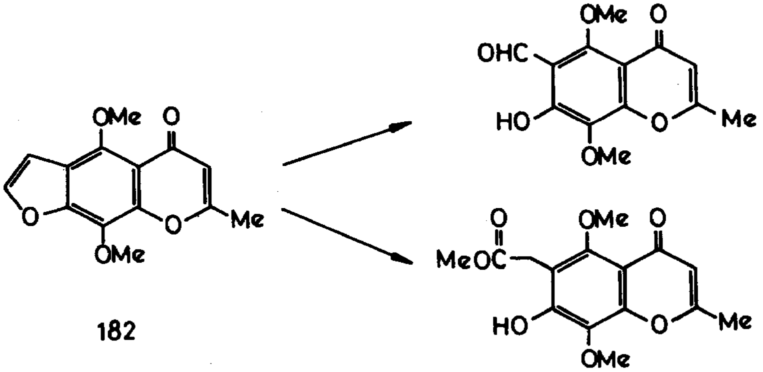


181

Oxidation of the benzofurane derivative (182) (khellin) by $NaIO_4$ in the presence of OsO_4 afforded the hydroxyaldehyde (183). Using $O_2/PdCl_2/CuCl$ catalytic oxidation the hydroxyester (184) was obtained [454].



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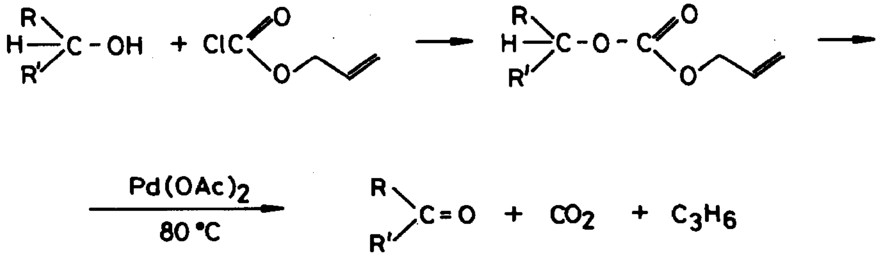
Oxygen inhibited secondary reactions of AcOOH in the oxidation of acetaldehyde in the presence of Co^{2+} ions [455].

Alcohols may be oxidized to aldehydes or ketones using the following sequence of reactions [456]:



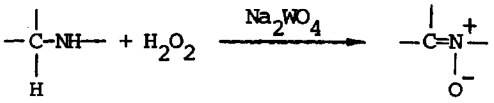
Pt complexes catalyze the oxidation of primary alcohols by I_2 in the presence of water to give carboxylic acids which are present as esters. Unsubstituted Pt halide complexes like PtX_6^{2-} or PtX_4^{2-} (X = Cl, Br, I) were the most active [457].

The oxidation of ascorbic acid by tris(oxalato)cobaltate(III) in aqueous solution is catalyzed by Cu(II). The rate law of the reaction suggests a mechanism involving a copper-ascorbate complex [458].

See also [469, 531].

d) Oxidation of N-containing Organic Compounds

Tungstate catalyzes the oxidation of secondary amines to nitrones by H_2O_2:

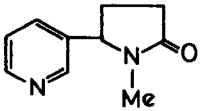


$$-\underset{\substack{| \\ H}}{\overset{|}{C}}\text{-NH-} + H_2O_2 \xrightarrow{Na_2WO_4} -\overset{|}{C}{=}\underset{\substack{| \\ O^-}}{N^+}-$$

(40–89%)

Other catalysts such as $VO(acac)_2$, $Ti(OBu)_4$ and $MoO_2(acac)_2$ are somewhat less effective [459].

The hydroxylation of acetanilide using catechol + Fe(III) + H_2O_2 systems has been studied using different substituted catechols. The highest yield of the three isomeric (*o*-,*m*-,and *p*-) acetamidophenols (6.7%) was obtained with 3,5-di-tBu-catechol [460]. Oxidation of $(PhCH_2)_2NNO$ by PhIO, $3\text{-}ClC_6H_4C(O)OOH$, and tBuOOH in the presence of (TPP)FeCl and (TPP)MnCl gave PhCHO and $PhCH_2OH$. These systems served as models for the cytochrome P450 dependent monooxygenases [461]. Kinetics of the Ru(III)-catalyzed oxidation of acetanilides by potassium iodate in aqueous AcOH at constant ionic strength are first order in Ru^{3+}, zero order in HIO_3, and complex order in *p*-RC_6H_4NHAc (R = H, Me, Cl, NO_2). The products of the reaction are *o*- and *p*-benzoquinone if R = H and the corresponding *o*-benzoquinones if R ≠ H [462]. The Ru(III)-catalyzed oxidation of 4-aminobutyric acid by alkaline hexacyanoferrate(III) ions was investigated. According to kinetic measurements the mechanism involves the formation of a Ru(III)-substrate complex which decomposes to a Ru(III) hydride and succinic acid in the rate determining step [463]. Oxidation of isoleucine and glutamic acid by $Fe(CN)_6^{3-}$ with $RuCl_3$ as catalyst was found to be first order in catalyst and zero order in oxidant. A mechanism involving hydride ion transfer from the amino acid α-carbon to Ru(III) was proposed [464]. Nicotine was oxidized to the lactame (185) by $NaIO_4$ in the presence of RuO_2 [465].



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Amino acids were oxidized to aldehydes by alkaline $[Fe(CN)_6]^{3-}$ in the presence of Os(VIII) catalyst. The reaction proceeds through formation of a transient amino acid complex with $[OsO_4(OH)_2]^{2-}$ [466].

A free radical mechanism was proposed for the oxidation of glycine by $S_2O_8^{2-}$ catalyzed by Cu^{2+}. The reaction was first order in oxidant and zero order in substrate [467]. The kinetics of oxidation of $tBuNHNH_2$ by tris(dimethylglyoximato)nickelate(IV) in the presence of aqueous Cu(II) was determined. The reaction involves an intermediate complex between Cu(II) and the substrate. Oxidation products are N_2 and tBuOH [468].

See also [469].

e) Oxidation of P-, S- or Halogen-containing Organic Compounds

Iron(II)-induced oxidations with H_2O_2 were studied in anhydrous acetonitrile. Monooxygenations and dehydrogenations take place if H_2O_2 is slowly added to a solution containing Fe^{2+} and the organic substrate (olefins, alcohols, aldehydes, ketones, hydrazobenzene, Ph_3P, PhI, sulfoxides). Dioxygenations are characteristic for the system if Fe^{2+} is added to a solution of H_2O_2 and the substrate [469]. The reduction of tBuOOH by triphenyl phosphite is catalyzed by the Ni(II) salt of O,O-diisopropyl dithiophosphoric acid [470]. A modified Sharpless reagent composed of $Ti(OPr^i)_4$ + 2 diethyl tartrate + H_2O + 2 tBuOOH homogeneously oxidized sulfides to sulfoxides. The optical yields ranged from 4 to 93% with the highest being observed in the case of methyl p-tolyl sulfoxide [471]. Organic sulfides, dissolved in nitromethane, may be oxidized to sulfoxides with aqueous nitric acid in the presence of $Bu_4N^+AuCl_4^-$

as oxidation and phase-transfer catalyst. The oxidation of the thio group is selective and may be carried out also if the molecule contains other oxidizable groups such as tertiary amino, hydroxy, etc. [472]. Rate constants and activation parameters were determined for the oxidation of MePhSO by chloramine-T catalyzed by Os(VIII) [473].

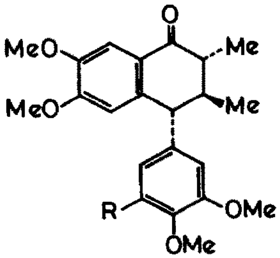
Oxidation of allyl chloride with H_2O_2 catalyzed by sodium tungstate was found zero order in oxidant and first order in substrate and catalyst [474]. Several Mo compounds were tested as catalysts for the epoxidation of allyl chloride with tBuOOH to epichlorohydrin. The most efficient were molybdenum abietate, a Mo complex with tBuOOH and EtOH, and a compound prepared from decyl alcohol and MoO_3 [475].

6. Stoichiometric Oxidation of Organic Compounds with High Valent Transition Metal Complexes

a) Oxidation of Hydrocarbons or Hydrocarbon Groups

Organometallic peroxides like $(tBuO)_2MOOBu^t$ [M = Al,VO] oxidize C_5 - C_{10} n-alkanes to the corresponding secondary alcohols and/or ketones, 1-octene to 1,2-epoxyoctane or sec. octenols, Bu_2O to PrCHO acetals, and PhMe, PhOMe and mesitylene to the corresponding phenols in > 99% yield [476].

Kinetics of the oxidation of succinic acid by chromic acid at very high concentration of perchloric acid were first order in oxidant and second order in substrate [477]. Oxidation of cholesterol with pyridinium chlorochromate in CH_2Cl_2 containing $CaCO_3$ at 25°C gave 91% cholest-5-ene-3-one [478]. Oxidation of 1-aryl-1-propenes with CrO_3 + HBF_4 + MeCN or CrO_3 + $HClO_4$ + MeCN gave the 4-aryltetralones (186) (R = H, MeO) [479].



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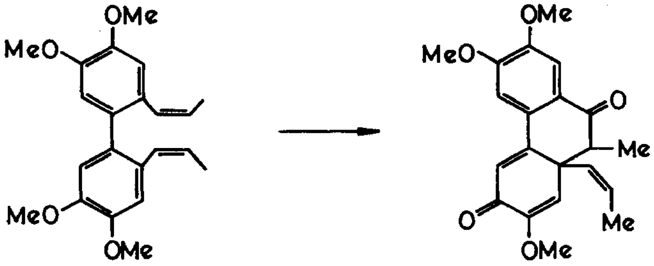
Oxidation of (187) with the $CrO_3 + HBF_4 + MeCN$ reagent gave (188) [480].



187 188

Phenyl alkyl ketones were photo-irradiated in the presence of $K_2Cr_2O_7$ or $KMnO_4$ to yield 1,4-dicarbonyl compounds regiospecifically:

$$PhC(=O)(CH_2)_3R \longrightarrow PhC(=O)CH_2CH_2C(=O)R$$

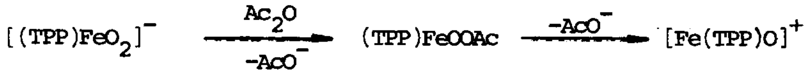
Treatment of 2-octanone in the same way afforded a mixture of 2,5- 2,6- and 2,7-octadiones [481]. Reaction of $ClCrO_2^+$ with ethene in a selected ion flow tube gives product ions deriving both from oxygen transfer (epoxide) and from cleavage of the alkene (formaldehyde and a Cr(VI)-oxo carbene) [482].

Substituted biphenylenes were oxidized in AcOH with $Mn(OAc)_3$. Methyl substituents were oxidized to formyl and acetoxymethyl groups, the oxidation of other derivatives yielded nuclear acetoxymethylated products [483]. The oxidation of α, β-unsaturated ketones with $Mn(OAc)_3$ in refluxing benzene furnishes α'-acetoxyenones (189) in good yields [484].

189

Oxidation of dialkyl malonates by manganic pyrophosphate in aqueous AcOH was studied. The results were consistent with a Michaelis-Menten type kinetics [485]. Treatment of alkenes with cetyltrimethylammonium permanganate in CH_2Cl_2 at 20° gave the corresponding cis-dihydroxy compounds in good yields. PhCOCOPh was formed in the reaction of PhC$\equiv$CPh and the oxidant [486]. The oxidation of NaOAc to oxalate by MnO_4^- in alkaline and neutral media was first order with respect to both acetate and MnO_4^- [487]. Yields of cis-1,2-cyclohexanediol formed by the reaction of a MeOH/water solution of $KMnO_4$ with cyclohexene increased from nearly zero to 84% with stirring efficiency and dilution. This was attributed to the formation of an intermediate hypomanganate ester which is hydrolyzed by water to glycol but is further oxidized by excess MnO_4^- [488].

Phenanthrene is hydroxylated at the 9-position by $Fe(CN)_6^{3-}$ in 90% aqueous acetic acid. The oxidation proceeds via formation of a radical cation intermediate [489]. Oxidation of xylenes by acidic $Fe(CN)_6^{3-}$ giving aldehydes as major products is first order each in substrate, oxidant, and acid. A radical intermediate was detected by ESR spectroscopy [490]. The peroxo complex $[Fe(TPP)O_2]^-$ oxidizes alkanes to alcohols only in the presence of an acylating agent (Ac_2O). The active species is $[Fe(TPP)O]^+$ which is formed according to the following stoichiometry:

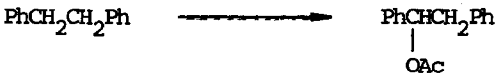


$$[(TPP)FeO_2]^- \xrightarrow[-AcO^-]{Ac_2O} (TPP)FeOOAc \xrightarrow{-AcO^-} [Fe(TPP)O]^+$$

This chemical system is at present the best model of cytochrome P-450 [491]. Oxidation of cyclohexene was studied using the systems $Fe(TPP)O_2 + Ac_2O$ and $Fe(TPP)Cl + AcOOH$. The peroxo complex yields cyclohexenol-1 and cyclohexene oxide; with the peracid only cyclohexene oxide is formed. The oxidation of cyclohexane with the $Fe(TPP)Cl + (RCO)_2O$ system is independent of the nature of the anhydride. The oxoferrylporphyrine cation radical $[Fe(TPP)(O)]^+$ is responsible for these oxidations [492]. When aqueous solutions of sulfuric acid containing benzene and iron(III) sulfate were irradiated, low but reproducible amounts of phenol were obtained. Phenol formation increased with increasing Fe^{3+} concentration and was higher in weakly acidic (pH $\approx$ 3.5) solutions [493].

The kinetics of oxidation of trans-cinnamic acid by ruthenate and perruthenate ions was studied [494]. Allylic alcohols and their ethers were subjected to oxidation by OsO_4. The main product had in all cases erythro configuration with respect to the preexisting OH or OR group and the adjacent new OH group [495].

Oxidation of various aryl-conjugated olefins like styrene with $Co(OAc)_3$ in wet AcOH under N_2 gives the corresponding glycol monoacetates in good yield [496]. Cobalt(III) acetate oxidizes 1,2-diphenylethane in acetic acid to the side-chain substituted product (190):



$$PhCH_2CH_2Ph \longrightarrow \underset{\displaystyle OAc}{PhCH}CH_2Ph$$

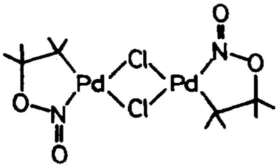
190

$PhCMe_2CMe_2P$

191

No reaction occurs in the case of (191) indicating that side-chain acetoxylation starts with H atom abstraction from the α-position [497].

Alkenes are stoichiometrically, and in the presence of air, catalytically oxidized by $(MeCN)_2Pd(NO_2)Cl$. Depending on the structure of the olefin, ketones, allyl alcohols, α,β-unsaturated ketones, or epoxides are being formed, in some cases with good selectivity. Heterometallacyclopentane complexes of type (192) are formed as intermediates [498].

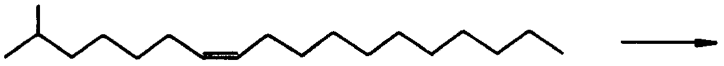


192

See also [388].

b) Epoxidation of Olefins

Stoichiometric epoxidation of (193) to form disparlure (194) was carried out with MoO_5L complexes. If L = Me_2(-)-2-piperidino succinate 57% yield of (+)-(194), if L = Me_2(-)-2-morpholinosuccinate 39-46% yield of (-)-(194) was obtained [499].



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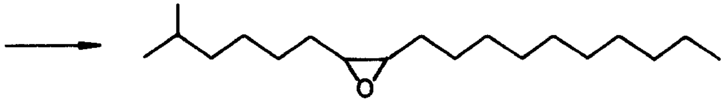
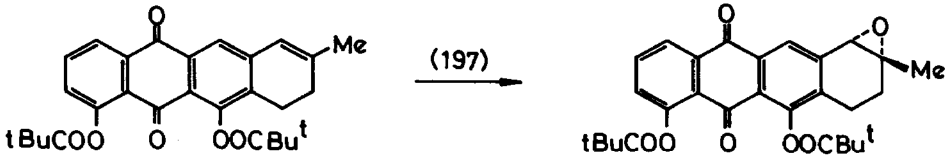
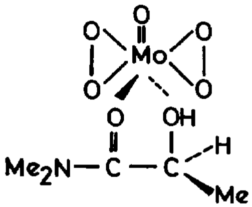


194

The interaction of $(tBuNC)_2NiO_2$ and $MoO_2Br_2(OPPh_3)_2$ with cyclohexene leads first to cyclohexene epoxide which is then transformed by excess of Mo complex into 1,2-dibromocyclohexene. Epoxidation is performed probably by a Mo peroxo complex, formed by dioxygen ligand transfer from Ni [500]. The tetracyclic olefin (195) was enantioselectively epoxidized to (196) with 53% o.y. using the stoichiometric reaction with a Mo(VI)-oxodiperoxo complex (197) containing (S)-dimethyl lactamide [501].



195 196



197

The "oxo-like" Mn porphyrin complex Mn(TMP)(O)Cl (TMP = = tetramesitylporphyrinato) obtained from Mn(TMP)Cl and NaOCl, stoichiometrically oxidizes styrene and PPh_3 to styrene oxide and $OPPh_3$, respectively. The complex is also an effective catalyst for styrene epoxidation with NaOCl under phase transfer conditions [502]. See also [498, 482].

c) Oxidation of O-containing Functional Groups

The kinetics of oxidation of diethylene glycol by vanadium(V) in acidic solutions was examined. A radical mechanism was proposed [506]. The rate law for the oxidation of 2-ethyl-1,3-hexanediol by vanadium(V) in water-dioxane medium was first-order in V^{5+}, third-order in H^+, and first-order in substrate [504]. The kinetics of oxidation of 2-hydroxycarboxylic acids with vanadium(V) were studied in perchloric acid solutions. The reactivity increased in the order glycolic acid < lactic acid < malic acid < tartaric acid [505].

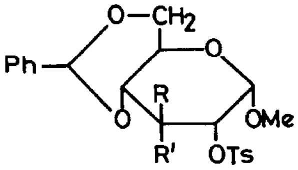
The reaction rates of oxidation of benzyl alcohol by chromic acid were similar in aqueous solution and in a two-phase system containing a phase-transfer agent. The two-phase system prevented further oxidation of PhCHO to the acid [506]. The oxidation of D-galactose, D-xylose, and L-arabinose by chromium peroxydichromate in diluted H_2SO_4 is first order each in substrate, oxidant, and H_2SO_4 [507]. Alcohols are oxidized to aldehydes or ketones and thiols are oxidized to disulfides by tetrabutylammonium chlorochromate $(Bu_4N)(CrO_3Cl)$ at room temperature. The new reagent is especially useful for the oxidation of benzylic or allylic alcohols [508]. Regioselective oxidation of partially acetylated aldohexopiranosides was carried out with pyridinium chlorochromate [509]. The kinetics of oxidation of several diols with pyridinium chlorochromate were studied in DMSO. Kinetic isotope effects, activation energies, and entropies were determined [510]. The OH groups in collagen were oxidized to carbonyl groups by pyridinium chlorochromate [511]. Oxidation of the allyl alcohol (198) by pyridinium chlorochromate in CH_2Cl_2 followed by treatment with MnO_2/NaCN/AcOH -MeOH at room temperature furnished the ester (199) in 75% yield [512].

198 199

Pyridinium chlorochromate oxidizes 5,6-dihydropyrans (200) to α, β-unsaturated δ-lactones (201) with good to excellent yields [513].

200 201

Selective oxidation of secondary alcohols in the presence of primary ones has been achieved by (a) protection of primary alcohols by $tBuMe_2SiCl$, (b) oxidation of secondary alcohols by pyridinium fluorochromate or benzyltrimethylammonium chlorochromate, and (c) deprotection of primary hydroxyls [514]. The oxidation of alcohols (benzyl, ethyl, cyclohexyl) in $MeCN/PhNO_2$ by pyridinium fluorochromate was found to be first order with respect to oxidant and independent of substrate concentration [515]. Oxidation of (202) with pyridinium dichromate and Ac_2O gave the corresponding carbonyl derivative (203). The method is generally useful for the oxidation of alcohols [516].

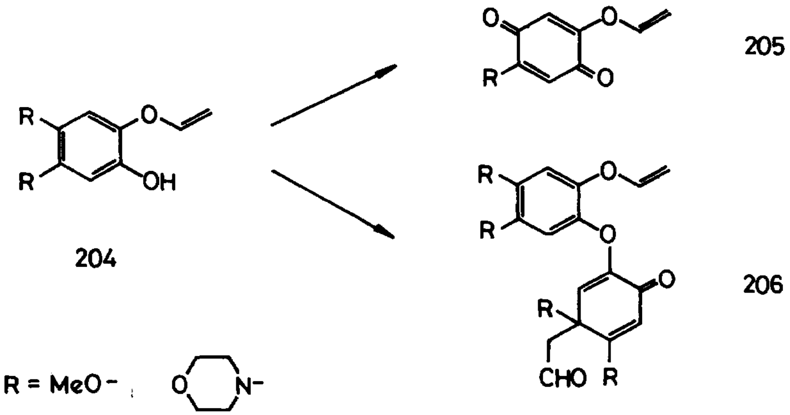


202; R = OH, R' = H

203; RR' = O

The induced oxidation of oxalic acid or oxalate monoanion by Cr(VI) + Fe(II) involves the formation of Cr(V) by one-electron transfer from Fe(II); Cr(V) then oxidizes the acid to CO_2 via $^{\bullet}OOCCOO^-$. Mn(II) has an inhibitory effect on the reaction [517]. Mn(IV) solutions prepared from $MnO(OH)_2$ and phosphoric acid oxidize propane-1,2-diol to formaldehyde and acetaldehyde. The reaction shows autocatalytic behavior which can be explained by the observation that Mn(III) enhances the reaction rate [518]. The rate of oxidation of mandelic acid by Mn(III)pyrophosphate, conducted in aqueous AcOH or aqueous dioxane, decreased with increasing proportions of AcOH or dioxane [519]. The reactivity of different organic compounds against oxidation by $KMnO_4$ has been determined spectrophotometrically. The most active were p-benzoquinone, mesityl oxide and aniline, the least active were caprolactam, cyclohexanone and cyclohexanol [520]. The kinetics of the oxidation of diols and their monoethers by acidic MnO_4^- were studied. $HMnO_4$ was found to be the reactive oxidizing agent. An acyclic mechanism was proposed for the oxidation of vicinal diols [521]. The kinetics of oxidation of ribose by $KMnO_4$ in the presence of acid was determined [522]. The pseudo-first-order rate constant of the oxidation of benzaldehyde with $KMnO_4$ was determined by flow injection analysis [523]. Cetyltrimethylammonium permanganate was found to be a highly selective reagent for the oxidation of benzylic alcohols to the corresponding aldehydes or ketones. Oxidation was carried out in dichloromethane solution at 30°C and yields were 90-98% [524].

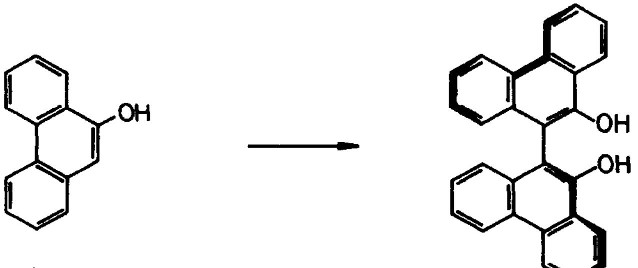
Kinetic parameters for the oxidation of pentoses and hexoses by Fe^{3+} in H_2SO_4 at 100-130°C were determined [525]. Monosaccharides were oxidatively degraded to monosaccharides with less carbon atoms by $FeCl_3$ under irradiation with near-UV to visible light. The degradations were shown to proceed via formation of an Fe(III)-monosaccharide complex [526]. Oxidation of glyceraldehyde phosphate with $Fe(CN)_6^{3-}$ at pH 8-11.5 was first order in the substrate and gave $^{2-}O_2P(O)OCH_2CH(OH)CO_2^-$ via a radical-anion mechanism [527]. The oxidation of D-galactose by $Fe(CN)_6^{3-}$ in the presence of ethylenediamine follows zero order kinetics with respect to $Fe(CN)_6^{3-}$ and first order both with respect to sugar and OH^-. Probably the rate of enolization is rate determining [528]. In a study of oxidative coupling of phenols the oxidation of resorcinol and orcinol with alkalic $Fe(CN)_6^{3-}$ was found to be first order each in substrate, oxidant and alkali. A radical intermediate was observed [529]. 2-(Vinyloxy)phenols (204) were oxidized by $FeCl_3$ or $K_3Fe(CN)_6$ to the corresponding quinones (205) and with AgO or Ag_2O to the dimers (206) [530].



Oxo complexes of Ru(VI) and Ru(VII) were used to oxidize organic compounds. Thus RuO_4^{2-} and RuO_4^- oxidize primary alcohols to carboxylic acids and secondary alcohols to ketones. $(Ph_4P)(RuO_2Cl_3)$ and $RuO_2(bpy)Cl_2$ cleanly oxidize a wide range of alcohols to aldehydes and ketones without attack on the double bond. RuO_4^{2-} catalyzes the oxidation of alcohols by $S_2O_8^{2-}$ [531]. Ruthenium dioxide hydrate oxidizes allylic alcohols to unsaturated carbonyl compounds and also effectively catalyzes the same oxidation with air as an oxidant at 70° in dichloroethane as solvent. The oxidation proceeds with retention of olefin stereochemistry, thus geraniol (207) is transformed into citral consisting of 97.5% of the E-isomer aldehyde (208) [532].

The rate of L-ascorbic acid oxidation by $Co(NH_3)_6^{3+}$ is first order with respect to both the substrate and the oxidant [533]. The kinetics of oxidation of benzaldehyde and some substituted benzaldehydes by $Na_2IrCl_6.6H_2O$ were studied. The large deuterium isotope effect indicates that the cleavage of the aldehydic C-H bond is the rate-determining step [534]. The kinetics of oxidation of ascorbic acid by tris(dimethyl-glyoximato)nickelate(IV) was investigated. The reaction is of pseudo first order and the mechanism involves a rate-determining outer-sphere one-electron transfer [535].

Rate constants and activation parameters were determined for the oxidation of furfural by Cu^{2+}, Fe^{3+}, Ce^{4+}, Ag^{+}, Hg_2^{2+} and Hg^{2+}. A one-electron mechanism was proposed for the first three of these cations and a two-electron mechanism for the other cations [536]. The kinetics of oxidation of dihydroxyfumaric acid to diketosuccinic acid by Cu^{2+} was studied [537]. Butanone-2- and cyclohexanone were oxidized by $K_5[Cu(H_2TeO_6)_2]$ in aqueous alkaline medium. The kinetic evidence leads to the conclusion that the rate-limiting step is the one-electron reduction of Cu(III) to Cu(II) [538]. Oxidative coupling of 9-phenanthrol (209) with a (-)-(R)-1,2-diphenylethylamine-Cu(II) complex yielded (-)-(S)-10,10'-dihydroxy-9,9'-biphenanthryl (210) in 86% preparative yield and 98% optical purity [539].



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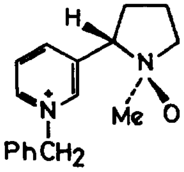
210

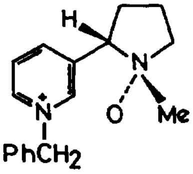
See also [30, 405].

d) Oxidation of N-containing Organic Compounds

The stereoselective oxidation of 1-benzylnicotinium bromide with peroxomolybdate and peroxotungstate gave *cis*- and *trans*-1'-N--oxides (211a) and (211b) in the ratio of 14:1 and 15:1, respectively [540].

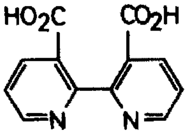


211a



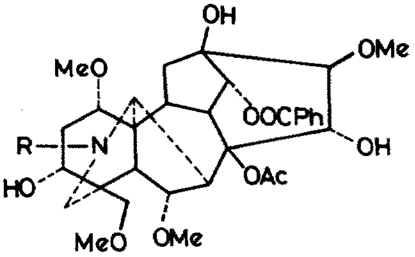
211b

Based on kinetic measurements, a mechanism was proposed for the oxidation of leucine by manganic sulfate in acidic medium [541]. The kinetics of the oxidation of L-arginine by $KMnO_4$ in moderately concentrated sulfuric acid has been determined. The oxidation is acid catalyzed. A mechanism was proposed [542]. Colloidal MnO_2 species participate in the MnO_4^- oxidation of Me_2NH by acting as a heterogeneous catalyst. Due to this simultaneously a homogeneous and a heterogeneous oxidation reaction take place. Mechanisms were proposed for both reactions [543]. 2,2'-Binicotinic acid (212) was prepared by refluxing the water solution of phen with NaOH and $KMnO_4$ [544].



212

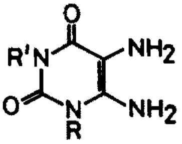
An isotopic labeling study has shown that the N-formyl group of oxonitine (213), a product of $KMnO_4$ oxidation of aconitine (214) originates from the methylene group of the N-ethyl of aconitine [545].



213, R = CHO

214, R = CH_2CH_3

Oxidation of L-adrenaline and of L-dopa in the presence of $FeL(OH)_2^+$ ions (L = 2,2':6'2":6"2"'-tetrapyridyl) bound to poly(L-glutamate) or to poly(D-glutamate) was studied. The rate--determining transfer of electron from the substrate to the central metal ion proceeded in some cases stereoselectively [546]. The electron-transfer from 1-benzyl-1,4-dihydronicotinamide, a NADH model compound, to FeL_3^{3+} (L = bpy, phen) was investigated in MeCN. The nicotinamide derivative acted as a one-electron donor in the absence of base whereas in the presence of a base it acted as a two-electron donor [547]. The oxidation of 5,6-diaminouracil (215) (R, R = H, Me) with $FeCl_3$ gave pyrimido pteridinetetrones (216) in good yield [548].



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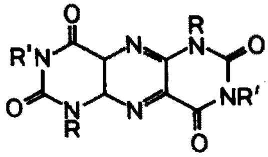
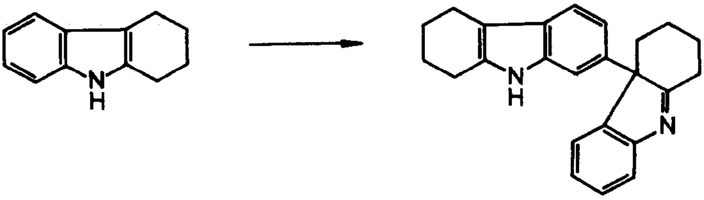


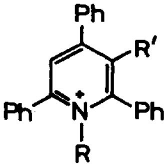
216

Ferric chloride oxidizes 1,2,3,4-tetrahydro-9H-carbazole (217) to (218) in 5% yield [549].



217 218

The oxidation of trimethylamine by $Fe(CN)_6^{3-}$ in aqueous medium gave formyldimethylamine and was first order both in the substrate and the oxidant [550]. Ferricyanide ion oxidation of acridine species formed by disproportionation of 10-methylacridinium cation is kinetically first order in each $Fe(CN)_6^{3-}$ and total acridine species. The reaction rate is pH-dependent [551]. The pyridinium salts (219) (R = Me, Ph; R' = Me, Et, Ph) were oxidized by $K_3Fe(CN)_6$ in aqueous KOH and EtOH to give pyrroles (220) (R = Me, Ph; R' = Me, Et, COPh) [552].



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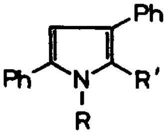
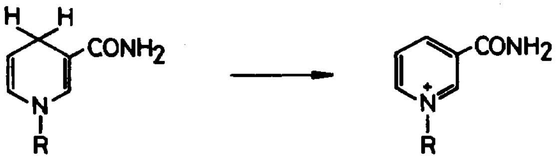


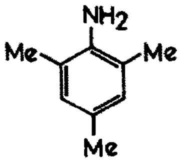
220

The kinetics of the oxidation of N-substituted dihydronicotinamides PyH_2 (221) by $Fe(CN)_6^{3-}$ into the corresponding pyridinium derivatives Py^+ (222) was studied. The proposed mechanism involves PyH_2^+ and $PyH^•$ species as intermediates [553].



221 222

The oxidation of mesidine (223) in methanolic media by ferricyanide, dichromate and persulfate afforded an anil (224) containing a shifted methoxymethyl group in addition to the principal product (225) formed by oxidative dealkylation [554].



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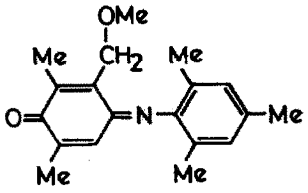

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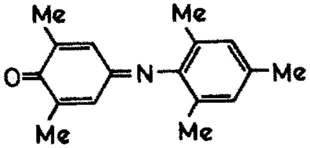


225

The kinetics and mechanism of the oxidation of NADH by ferrocenium cation and several substituted ferrocenium cations was reported. The results were consistent with a rate-limiting one-electron transfer [555].

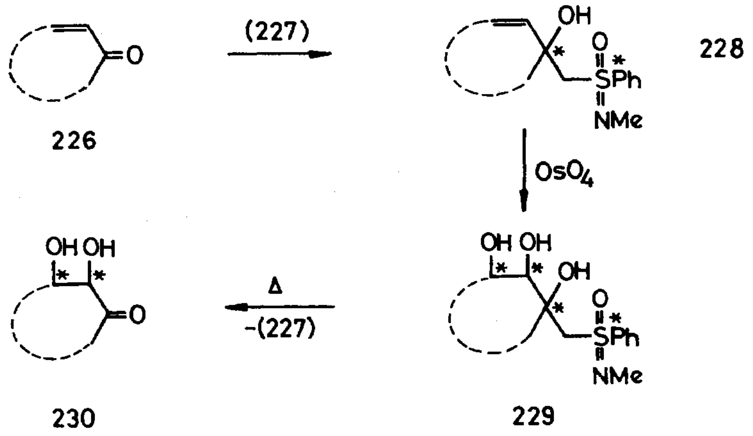
Aromatic primary amines were oxidized using $AgNO_3$ or AgOAc to give azobenzene derivatives in 11-25% yield [556].

See also [520].

e) Oxidation of P-, S- or Halogen-Containing Organic Compounds

Phosphorous ylides $R_3P{=}CH_2$ are oxidized by $CuCl_2$ in anhydrous THF at low temperature to ethylidene-1,2-bis-phosphonium salts $R_3P^+{-}CH_2CH_2{-}P^+R_3$ [557].

Aromatic thiols were oxidized to disulfides by pyridinium chlorochromate [558]. The stoichiometry, kinetics and mechanism of the Cr(VI) oxidation of L-cysteine have been studied. L-Cystine and Cr(L-cysteinato)$_2^-$ were the sole products. The preferred mechanism involves the formation of a chromate thio ester followed by a two-electron reduction of Cr(VI) and formation of L-cystine [559]. The oxidation of the 1,2,3,4-thiatriazol-5-thiolate ion $CS_2N_3^-$ by MnO_4^- was studied [560]. Enantiomerically pure dihydroxycycloalkanones (230) were prepared from cycloalkenones (226) by transforming these first with (S)-N,S-dimethyl-S-phenylsulfoximine (227) into the adducts (228) and hydroxylating the individual diastereomers of (228) with OsO_4. The resulting triols (229) were thermally decomposed into (227) and (230) [561].



A kinetic study of the oxidation of cysteine, cysteine methyl ester, and penicillamine by Cu(II)-2,9-dimethyl-1,10-phenantroline (dmp) complexes was reported. The results are consistent with two parallel pathways in which oxidation of coordinated sulfur occurs within 1:1 thiol complexes of $Cu(dmp)_2^{2+}$ and $Cu(dmp)^{2+}$ [562].

1-Chlorindan was oxidized by $Na_2Cr_2O_7$ in aqueous H_2SO_4 to give 1-indanone [563].

See also [502, 508].

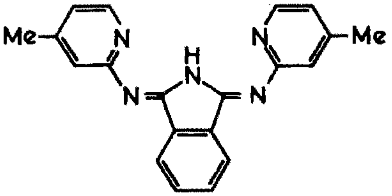
7. Coordination Chemistry Related to Oxidation

The crystal structures of two Ti tartrate asymmetric epoxidation catalysts [containing (R,R)-N,N'-dibenzyltartramide and (R,R)-diethyl tartrate, respectively] were determined [564]. The structure of $RuBr_2(Me_2SO)_4$, a selective sulfide oxidation catalyst using O_2, was determined [565]. Several Pd(II) nitrile, alkene and hetero-metallacyclopentane complexes involved in metal nitro catalyzed alkene oxidation reactions were prepared and characterized [566]. The intermediate complex (231) formed during oxidation of norbornene with O_2 using $PdCl_2NO_2(MeCN)_2$ catalyst is transformed in the presence of $CuCl_2$ into (232) and its thermal decomposition into epoxynorbornane is completely suppressed [567].

231 232

8. Electrooxidation

The Ru(IV) complex $[Ru(trpy)(bpy)(O)]^{2+}$ (trpy = 2,2',2"-terpyridine) can be used as a catalyst for the electrocatalytic oxidation of alcohols, aldehydes, and C-H bonds adjacent to olefinic or aromatic groups. The Ru(IV) complex is regenerated by the electrochemical oxidation of $[Ru(II)(trpy)(bpy)(H_2O)]^{2+}$ [568]. The Ru complex $LRuCl_3$ (L = 233) catalyzes the autoxidation and electrochemical oxidation of alcohols in basic alcoholic solution. The principal products are aldehydes and ketones. The catalyzed electrochemical oxidation was carried out in presence of lutidine [569].



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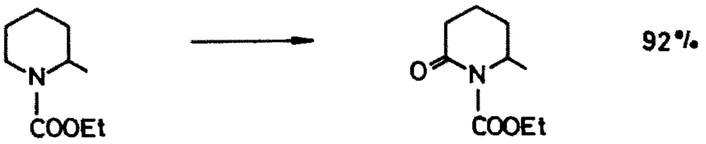
N-Proceted aliphatic amines like (234) could be electrooxidized in excellent yields into the corresponding amides using $RuO_2.2H_2O$ or $RuCl_3$ in a saturated NaCl-acetone system. The active oxidizing agent is RuO_4 [570].



234

Electrooxidation of 4-methylpyridine and 2,6-dimethylpyridine with Ag(bpy)$^+$ in propylene carbonate as solvent was studied. The reactions involve mixed Ag(II) bpy-methylpyridine complexes [571].

V. Reviews

Homogeneous catalysis by transition metal complexes. 250 refs. [572].

Homogeneous catalysis of organic reactions by complexes of metal ions. 237 refs. [573].

Catalysis of transition metal complexes under phase transfer conditions. 58 refs. [574].

Noble metal catalysts in the manufacture of organic compounds. 28 refs. [575].

Platinum metal complexes as catalysts. [576].

Catalysis by complexes with palladium-palladium bonds. [577].

The catalytic activity of some Rh(I) compounds. 38 refs. [578].

Basic principles of the catalysis of conversions of unsaturated hydrocarbons by clusters of metal carbonyls. 33 refs. [579].

Homogeneous catalysis with metal phosphine complexes. A historical introduction. 46 refs. [580].

Structurally characterized transition-metal phosphine complexes of relevance to catalytic reactions. 94 refs. [581].

Functionalized tertiary phosphines and related ligands in organometallic coordination chemistry and catalysis. 54 refs. [582].

Polydentate ligands and their effects on catalysis. 67 refs. [583].

Binuclear, phosphine-bridged complexes: progress and prospects. 153 refs. [584].

Polymer-bound phosphine catalysts. 150 refs. [585].

Gel-immobilized metal-complex catalysis. [586].

Technological perspectives for anchored catalysts. 12 refs. [587].

Hydrogen and carbon monoxide as ligand combination for transition elements. 75 refs. [588].

The impact of transition metal-based homogeneous catalysis in industrial processes. 14 refs. [589].

Platinum carbonyls and their use in homogeneous catalysis. 288 refs. [590].

Homogeneous catalytic hydrogenation of carbon monoxide: ethylene glycol and ethanol from synthesis gas. 219 refs. [591].

Factors which determine product selectivity in homogeneous hydrogenation of carbon monoxide to oxygenates. 190 refs. [592].

Supported clusters and mechanism of carbon monoxide reduction. 58 refs. [593].

Do we know the mechanism of hydroformylation? 30 refs. [594].

Hydrogenation and hydroformylation with $HCo(CO)_4$ and $HMn(CO)_5$: radicals or otherwise. 14 refs. [595].

Hydroformylation. 127 refs. [596].

Some aspects of hydrogen activation in hydroformylation. 32 refs. [597].

Hydroformylation of unsaturated fatty acids. 74 refs. [598].

Regeneration of hydroformylation catalysts. 112 refs. [599].

Hydrogenation and hydroformylation reactions using binuclear diphosphine-bridged complexes of Rh. 97 refs. [600].

Homogeneous catalysis: a wedding of theory and experiments. [601].

Recent advances in homologation: the effect of promoters. 26 refs. [602].

Coordination chemistry of the carbon dioxide molecule: biological, chemical, electrochemical and photochemical activation. 203 refs. [603].

New stoichiometric and catalytic organometallic chemistry with actinides. C-H Activation and phosphine/phosphite chemistry. 68 refs. [604].

The effect of net ionic charge on the catalytic behavior of metal hydrides. 15 refs. [605].

Cationic rhodium and iridium complexes in catalysis. 66 refs. [606].

cis-Alkyl and *cis*-acylrhodium and -iridium hydrides: model intermediates in homogeneous catalysis. 38 refs. [607].

Transition metal hydrides in homogeneous catalytic hydrogenation. 27 refs. [608].

Kinetics and mechanism of reversible insertion of olefins and acetylenes into early transition metal-hydride bonds. 29 refs. [609].

Hydrogenation of vegetable oils by transition metal complexes. 131 refs. [610].

Organometallic catalysis in asymmetric synthesis. 67 refs. [611].

DIOP as a ligand in asymmetric catalysis using transition metal phosphine complexes. 60 refs. [612].

Asymmetric hydrogenation in the presence of bis diphenylphosphinic complexes of Rh. 25 refs. [613].

Asymmetric hydrogenation reactions using chiral diphosphine complexes of rhodium. 102 refs. [614].

Problems of asymmetric hydrogenation with complex catalysts. 47 refs. [615].

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Homogeneous asymmetric catalysis by means of chiral Rh complexes (hydrogenation and hydrosilylation). [617].

Hydrogenation reactions of carbonyl and C=N functions using Rh complexes. 97 refs. [618].

Catalytic hydrogen-transfer reactions. 131 refs. [619].

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Catalyzed ligand-phase oxidation of olefinic hydrocarbons. 118 refs. [627].

Metal nitro complexes as oxygen transfer agents: selective oxidation of organic substrates by molecular oxygen. 48 refs. [628].

Homogeneous catalysis of oxidation reactions using phosphine complexes. 148 refs. [629].

Oxidations with vanadium(V). 131 refs. [630].

Synthetic applications of palladium-catalyzed oxidation of olefins to ketones. 120 refs. [631].

List of Abbreviations

acac = acetylacetonate
Boc = t-butoxycarbonyl, tBuOC(O)-
BPPM = see Fig. (55)
bpy = 2,2'-bipyridine
COD = 1,5-cyclooctadiene
Cp = η^5-cyclopentadienyl
Cy = cyclohexyl
(-)-DIOCOL = see Fig. (8)
(-)-DIOP = see Fig. (7)
dmgH = dimethylglyoxime
DMSO = dimethylsulfoxide
dmpm = bis(dimethylphosphino)methane, $Me_2PCH_2PMe_2$
dpm = bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$
dppe = bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$
HD = 1,5-hexadiene
Ms = methylsulfonyl (mesyl), CH_3SO_2-
NBD = norbornadiene
nmen = neomenthyl
OEP = octaethylporphirinato
o.y. = optical yield
phen = 1,10-phenanthroline
salen = N,N'-bis(salicylidene)-ethylenediamino
SIL = silica
st = stearate, $nC_{17}H_{35}COO$
Tf = trifluoromethylsulfonyl (triflyl), CF_3SO_2-
tpm = triphenylphosphine m-monosulfonate, $PPh_2(C_6H_4SO_3^-)$
TPP = 5,10,15,20-tetraphenylporphirinato
Ts = p-toluenesulfonyl (tosyl) p-$CH_3C_6H_4SO_2$-

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