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Transition metals in organic synthesis: hydroformylation, reduction, and oxidation. Annual Survey covering the year 1992 *

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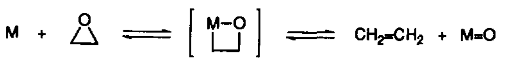
1. Theoretical calculations

Density functional calculations were carried out on the elementary steps of the hydroformylation reaction based on tricarbonylhydridocobalt. Geometries and relative energies were determined for intermediates involved in each elementary step [1]. A mathematical model was developed for steady-state multiplicity and limit cycles in a reaction that converts olefins and synthesis gas to aldehydes and alcohols in gas-sponged loop reactors with internal and external circulation loops [2].

An *ab initio* MO/SD-CI study of model complexes of intermediates in electrochemical reduction of CO_2 catalyzed by $NiCl_2$(cyclam) has been made. Calculations were carried out on $Ni^IF(NH_3)_4(\eta^1\text{-}CO_2)$, $[Ni^I(NH_3)_5(\eta^1\text{-}CO_2)]^+$, $[Ni^{II}F(NH_3)_4(\eta^1\text{-}CO_2)]^+$, $Ni^IF(NH_3)_4(\eta^2\text{-}CO_2)$, $[Ni^I(NH_3)_4(\eta^2\text{-}CO_2)]^+$, and $[Ni^I(NH_3)_5(\eta^2\text{-}CO_2)]^+$ [3].

Quantum chemical calculations on 2-metallaoxetanes for Cr, Mo, Fe, Co, Ni, Cu, and Ag have shown that metallaoxetanes are reasonable intermediates in epoxidation reactions of olefins and in deoxygenation reactions of epoxides.



For Cr, Mo, Fe, Co, and Ni the deoxygenation reaction seems to be favored, whereas for Cu and Ag the epoxidation is preferred [4]. Reaction mechanisms were generated for the catalytic epoxidation of olefins by graph-theor. methods [5].

Linear correlations were observed between semiempirical AM 1-derived adiabatic — but not vertical — ionization potentials and the log k_0 of ferricyanide-mediated oxidation of 3-substituted 1-methyl-1,4-dihydropyridines [6].

In an attempt to systematize transition metal complex-catalyzed oxidation of organic substrates a general scheme based on the role the metal plays in dioxygen activation and oxidation reactions has been developed. Examples from the literature and the authors' laboratory serve as illustrations of the suggested five classes [7].

Intermediates in the platinum-halo complex-catalyzed oxidation of PH_3 to trialkyl phosphites by alcohols were studied by using a CNDO method [8].

2. Hydroformylation and related reactions of CO

2.1. *Hydroformylation*

2.1.1. *Cobalt catalysts*

High-pressure cylindrical internal-reflectance was used to simultaneously measure the concentrations of infrared-observable metal complexes and reactant and product concentrations under high-temperature and high-pressure conditions in the cobalt-catalyzed hydroformylation of 1-hexene. Based on the spectra, the direct hydrogenation of the heptanoylcobalt species to form the heptaldehyde product was concluded [9]. The kinetics of hydroformylation of propene [10] and the isomer distribution of the products [11] using an unmodified cobalt carbonyl catalyst were studied in a temperature range of 110–150°C and a pressure range of 35–100 bar.

The catalytic hydroformylation of 1-heptene to octanal isomers (n-octanal/2-methylheptanal = 3.8) at 25°C using 28 bar dihydrogen and 2 bar carbon monoxide partial pressure and $EtOC(=O)Co(CO)_4$ as catalyst precursor has been demonstrated [12].

The catalytic activity of various Group 8 and 9 metal compounds in hydroformylation of 1-hexene at 100°C and 50 bar $CO:H_2 = 1:1$ was compared. Of the metals studied, the cobalt and rhodium compounds, both as chlorides and as carbonyls, were found to be the most active catalysts. The effect of triethylamine upon the alcohol selectivity was also compared [13]. The comparison of the hydroformylation of 1-hexene with $Co_2(CO)_8$ or $Sn[Co(CO)_4]_4$ at 150°C and 60 bar $CO:H_2 = 1:1$ showed a low catalytic activity of the Co–Sn complex.

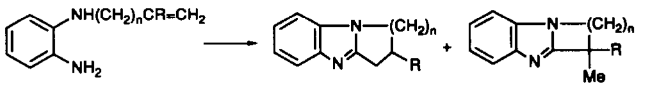
The normal/branched aldehyde ratios were 2.3 and 2.2, respectively [14].

The hydroformylation of 1-pentene in the presence of $Co_4(CO)_8P'_2(\mu_4\text{-}PPh)_2$ ($P' = PPh_3$ or $P(OMe)_3$) was studied using cylindrical internal reflectance spectroscopy [15]. Homogeneous hydroformylation of terminal alkenes at 130°C in the presence of $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PPh)_2$ or $Fe_2Co_2(CO)_{10}(\mu_2\text{-}CO)(\mu_4\text{-}PPh)_2$ was investigated [16]. Bisphosphine-cobalt-catalyzed hydroformylation of alkenes was investigated. The reactivity of the substrates decreased in the following order: cyclohexene > linear terminal alkenes > linear internal alkenes > diisobutene using catalysts obtained from cobalt(III) acetylacetonate and $(Ph_2P)_2CHMe$ or $(PhCH_2)_2PCH_2CH_2P(CH_2Ph)_2$ [17].

Phenylmethinyltricobalt enneacarbonyl and its Ph_3P, Ph_3As and Ph_3Sb derivatives were used as catalysts in hydroformylation. Hydroformylation products of styrene and di-isobutene were the completely normal aldehyde when using $PhCCo_3(CO)_8AsPh_3$ as the catalyst [18].

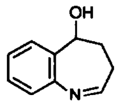
2.1.2. *Rhodium catalysts*

N-alkenyl-1,2-diaminobenzenes (**1**) gave benzimidazoles (**2** and **3**) in excellent yields in rhodium-catalyzed reactions with carbon monoxide and dihydrogen [19].



1 **2** **3**

The rhodium-catalyzed hydroformylation of *o*-propenylanilines gave 4,5-dihydro-3*H*-1-benzazepines together with small amounts of substituted 3-methylquinolines. *E.g.*: $2\text{-}H_2NC_6H_4CHOHCH{=}CH_2$ gives **4** as main product and ≤ 15% **5** [20].



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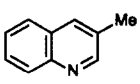
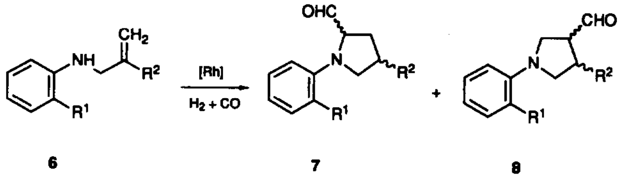


5

The $Rh_4(CO)_{12}$-catalyzed hydroformylation of some alkenyl phosphites such as $CH_2{=}CHCH_2CHROP(OEt)_2$ (R = H, Me, Ph) gave $MeCH(CHO)CH_2CH\text{-}ROP(OEt)_2$ with excellent regiocontrol at 50°C in benzene solution [21].

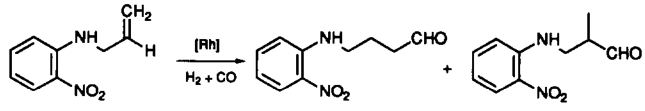
The $[Rh(OAc)_2]_2 + 4PPh_3$-catalyzed double hydroformylation of allylanilines (**6**) at 80°C and 28 bar $CO:H_2 = 1:1$ gave isomeric pyrrolidone aldehydes (**7**) and (**8**) through an enamine intermediate in up to 76% isolated yield.



6 **7** **8**

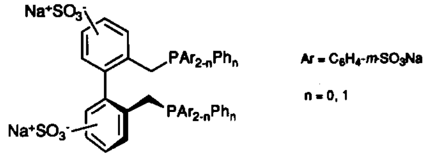
R¹, R² = H, Me; CN, Me; CN, H

From *o*-nitroaniline derivative **9** a mixture of aldehydes resulted in a single hydroformylation [22].



9 20% : 80%

The effect of olefin concentration in various solvents on the rate of 1-hexene hydroformylation at $p(CO) = p(H_2) = 10.3$ bar using $HRh(CO)(PPh_3)_3$ as the catalyst precursor was investigated [23]. Homobimetallic rhodium complexes with $Et_2P(CH_2CH_2)(Ph)PCH_2P(PH)(CH_2CH_2)PEt_2$ ligand were found to be surprisingly active and selective hydroformylation catalysts. Without adding any excess phosphine ligand > 25:1 linear-to-branched aldehydes were obtained from 1-hexene at 80°C and 4 bar pressure [24]. Exceptionally high n/iso ratios (up to 97% n) of butyric aldehyde were obtained in the rhodium-catalyzed hydroformylation of propene using **10** as a ligand in a two-phase system [25].



10

The use of n-heptanol + water biphasic systems for the $HRh(CO)(PPh_3)_3$-catalyzed allyl alcohol hydroformylation led to reduced catalyst inactivation and more efficient catalyst recycling in comparison with the homogeneous system [26].

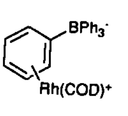
Carbonylhydridorhodium catalysts with Ph_3P, Ph_2EtP, $PhEt_2P$, Et_3P, and $(EtO)_3P$ ligands were compared in 1-butene hydroformylation with respect of their reactivity and selectivity. Complexes of strong σ-donating aliphatic phosphine ligands required a high temperature for their activation and showed a high aldehyde selectivity. In contrast, π-back-donation by triarylphosphines and particularly by phosphite esters led to a high normal-to-iso ratio of aldehydes but also led to more olefin hydrogenation and isomerization [27]. A correlation between the size of the natural bite angle of chelating diphosphines and the regioselectivity for formation of straight-chain aldehydes in the rhodium-catalyzed hydroformylation of 1-hexene was found [28].

Terpinolene, (*S*)-(−)-limonene, α- and β-cedrenes, α- and β-caryophyllenes and caryophyllene oxide were hydroformylated in the presence of $RhH(CO)(PPh_3)_3$ as the catalyst. Except for terpinolene the exocyclic double bonds were hydroformylated [29]. The hydroformylation of 1-hexene at 80°C and 10 bar $CO:H_2 = 1:1$ was studied using $Rh(acac)(CO)(PPh_3)$ as the catalyst precursor [30].

The homogeneous hydroformylation of styrene-butadiene copolymers in the presence of $RhH(CO)(PPh_3)_3$ was studied using infrared and ^1H and ^{13}C NMR spectroscopy. Both internal and *anti*-Markovnikov aldehyde products were observed [31]. Nitrile rubber with 40% acrylonitrile content was hydroformylated using *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(I) and $RhH(CO)(PPh_3)_3$ as catalyst at 90°C under 56 bar $CO:H_2 = 1:1$. The kinetics of the reaction show pseudo-first order dependence with respect to olefinic substrate and catalyst concentration [32].

New formyl-pregnene, formyl-androstene and the corresponding aminomethyl derivatives were synthesized selectively *via* hydroformylation using an *in situ* prepared rhodium-tributylphosphine catalyst at 120°C and 100–120 bar $CO:H_2 = 1:1$ [33]. Dicarbonyl (salicylaldoximato)rhodium complex was found to catalyze the hydroformylation of styrene at 60°C and 1 bar pressure in the presence of phosphines. The activity and selectivity increased as the phosphine ligands were changed from mono- to diphosphines. No side reactions such as hydrogenation were reported [34].

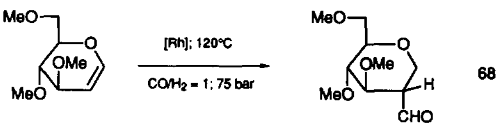
The zwitterionic rhodium complex **11** in conjunction with dppb as a catalytic system for the hydroformylation of α,β-unsaturated esters at 80°C and 40 bar $CO:H_2 = 1:1$ gave in excellent regioselectivity the branched-chain aldehydic ester [35].



11

Hydroformylation of 2-ferrocenylpropene using *in situ* prepared rhodium-phosphine catalyst at 100°C and 160 bar $CO:H_2 = 1:1$ gave the less-branched formyl isomer with more than 90% regioselectivity [36].

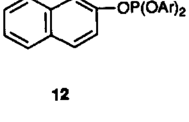
The complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2]$ has been shown to be an active precursor for the hydroformylation of terminal alkenes at 80°C and 8 bar $CO:H_2 = 1:1$ in the presence of an excess of PPh_3. The rate of the reaction increases with increasing $p(CO)$ and $p(H_2)$ up to a maximum. Further increase of $p(CO)$ and $p(H_2)$ results in lower reaction rates [37]. Under a pressure of 2 bar of $CO:H_2 = 1:1$ and 80°C, the hydroformylation of 1-hexene shows a half-order dependence on the catalyst, $[Rh(\mu\text{-}S^tBu)(CO)P(OMe)_3]_2$ concentration. This and the results of catalyst cross-over reactions provided evidence for an active species that is mononuclear [38]. The use of $[Rh_2\{\mu\text{-}S(CH_2)_3NMe_2\}_2(COD)_2]$ as catalyst precursor and tris(*o*-t-butylphenyl)phosphite as auxiliary ligand allowed the hydroformylation of glucal derivatives in good yields and selectivity, giving principally the α-formyl derivative [39]. *E.g.*:



The thiolato-bridged dinuclear rhodium complex $[Rh_2\{\mu\text{-}S(CH_2)_3NMe_2\}_2(COD)_2]$ was used as catalyst precursor for the hydroformylation of 2,3-dihydrofuran, 2,5-dihydrofuran, 3,4-dihydro-2*H*-pyran, and 3,6-dihydro-2*H*-pyran. Tetrahydrofuran-3-carbaldehyde was obtained in quantitative yield from 2,5-dihydrofuran at 80°C and 30 bar $CO:H_2 = 1:1$ in the presence of a tenfold molar excess of PPh_3. From the other olefins mixtures of aldehyde isomers were obtained [40].

The influence of modifying ligands in the $HRh\{P(OPh)_3\}_4$-catalyzed 1-hexene hydroformylation was studied at 5 bar pressure. The best results (75–85% yield of aldehydes) were obtained with the system $HRh\{P(OPh)_3\}_4 + Cp_2Zr(CH_2PPh_2)_2$ [41].

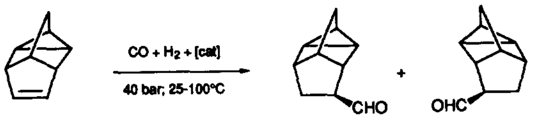
Asymmetric hydroformylation of vinyl acetate at 30–80°C and 100 bar $CO:H_2 = 1:1$ in benzene solution in the presence of an *in situ* prepared catalyst from $Rh(CO)_2(acac)$ or $[Rh(CO)_2Cl]_2$ and chiral bis(triarylphosphite) ligands *R*-**12** and *S*-**12** gave 2-acetoxypropanal in up to 95% regioselectivity and in 49% ee [42].



Ar = Ph, *p*-tolyl, 3,5-xylyl

12

Hydroformylation of **12** both in the presence of rhodium- and platinum-phosphine complexes afforded **14** selectively. In the case of optically active bisphosphines up to 22% ee-s were achieved [43].

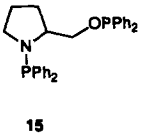


13 **S-14** **R-14**

See also [13,45,107].

2.1.3. Platinum catalysts

The regioselectivity and enantioselectivity of hydroformylation of *para*-substituted 2-phenylpropenes were investigated using [(*R*,*R*)-(DIOP)]Pt($SnCl_3$)Cl as the catalyst [44]. OrganOmetallic complexes of rhodium and platinum were used after electrochemical reduction for regio- and enantioselective olefin hydroformylation. The PtL_2Cl_2-$SnCl_2$ catalysts (L = phosphines) selectively hydroformylate α-olefins such as styrene or 1-hexene into linear aldehydes. With L-(+)-EPHOS [(1*R*,2*S*)-$Ph_2PNMeCHMeCPhOPPh_2$] as chiral ligand in the rhodium systems, asymmetric hydroformylation of styrene into hydratropaldehyde was observed in 95% yield and > 30% ee [45]. The complex Pt((*S*)-PROLOPHOS)Cl_2 (PROLOPHOS = **15**) in the presence of $SnCl_2$ was found to catalyze the hydroformylation of styrene to (*R*)-(−)-2-phenylpropanal with 37% optical purity [46].



15

See also [43,66].

2.1.4. Other metals as catalysts

The fluxional cluster anion $[HRu_3(CO)_8(PPh_2)_2]^-$ was found to catalyze the hydroformylation of olefins at 140°C and 25 bar (p(CO) = 15 bar, $p(H_2) = 10$ bar) and provides a mixture of aldehydes, alcohols and ketones. For ethene, the ratio of aldehyde to ketone to alcohol products can be varied between 90:2:8 and 29:70:1, depending upon the ethene partial pressure [47].

Homo- and hetero-bimetallic complexes containing bridging diphenylphosphido ligands have been screened as catalyst precursors for the hydroformylation of styrene at 120°C and 20 bar $CO:H_2 = 1:1$, and the hydrogenation of cyclohexanone at 140°C and 40 bar H_2. The most efficient precursor for the hydroformylation is $(CO)_3Ru(\mu\text{-}PPh_2)_2Fe(CO)_3$ giving 42% yield and 58% selectivity of the branched aldehyde. In the catalytic hydrogenation of cyclohexanone, the most active catalyst precursor was found to be the ruthenium-molybdenum complex $(CO)_3Ru(\mu\text{-}PPh_2)_2Mo(CO)_4$ leading to 56% yield of cyclohexanol [48].

See also [13].

2.1.5. Heterogeneous systems (supported complexes)

The impregnation of $[Ru_3(CO)_9(CCO)]^{2-}$ on silica gave a catalyst with high catalytic activity in ethene hydroformylation and CO hydrogenation. It was suggested that the ketenyl group is an active intermediate in the reaction [49]. The catalytic performance of ethene hydroformylation over $[H_xRu_3(CO)_9(CCO)]^{2-x}$ ($x = 0$–2) on $SiO_2 + Al_2O_3$, SiO_2 and MgO catalysts has been studied [50]. The MgO-supported catalyst was more active than those on SiO_2 or $SiO_2 + Al_2O_3$ [51].

The hydroformylation of α-olefins was studied using ruthenium and bimetallic catalysts prepared by cation-exchange of Na^+ in zeolites with Ru^{3+} and other transition metal ions. Precarbonylated Ru + Co + NaX (Ru : Co = 4 : 2) catalyst showed the best activity and selectivity at 200°C and 60 bar $CO:H_2 = 1:1$ [52]. The hydroformylation of cyclohexene using Ru^{III}–Co^{II} bimetallic complexes with P-, S-, or N-containing polymeric ligand supported on SiO_2 as the catalyst was investigated. The effects of reaction temperature, pressure, and Co/Ru ratio on the activities of the catalysts were studied [53].

The catalytic activity of silica-PPh_2-supported and unsupported $BrCCo_3(CO)_9$ in hydroformylation of 1-heptene was studied [54]. The cobalt cluster $PhCCo_3(CO)_9$ anchored to poly(benzyldiphenylphosphine styrene) and poly(benzyldiphenylarsine styrene) was used in 1-heptene hydroformylation. The normal–iso ratio and the aldehyde and alcohol selectivity were increased using the polymer-supported catalyst in comparison with using the parent cluster as the catalyst [55].

The silica-supported $K_2[Rh_{12}(CO)_{30}]$ cluster was found to be an active catalyst for the hydroformylation of ethene at atmospheric pressure [56]. Rhodium complexes immobilized on Ph_2P group-containing polystyrene were found to catalyze the hydroformylation of 1-dodecene at 10 bar $CO:H_2 = 1:1$ at 90°C. High yields of the unbranched aldehyde were obtained [57]. Immobilized rhodium catalysts obtained by attaching phosphites to a (co)polymer chain, show high activity towards the hydroformylation of the otherwise unreactive cyclooctene [58].

1-Hexene, other hexene isomers, and different olefins were hydroformylated using $Co_2Rh_2(CO)_{12}$ or a mixture of $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ supported on organic Dowex® resins, for the production of alcohols. In the case of 1-hexene at 100°C and 50 bar $CO:H_2 = 1:1$ pressure 95% and 99% alcohol yields were achieved with 0.7 and 1.1 straight to branched ratios, respectively. The presence of amino groups on the support or the addition of Et_3N to the hydroformylation reaction mixture seems to be essential for the single-step alcohol formation [59]. The direct synthesis of alcohols from 1-hexene using a reusable rhodium supported catalyst on crosslinked acrylic resins at 120°C and 120 bar $CO:H_2 = 1:1$ gave a close to one ratio of normal to branched products selectively [60]. In order to prepare alcohols in a single step hydroformylation of 1-hexene the optimum reaction conditions were investigated using $Co_2Rh_2(CO)_{12}$ as the catalyst supported on inorganic carrier materials. Best results were obtained with $Co_2Rh_2(CO)_{12}$ on alumina catalyst in the presence of Et_3N under 50 bar $CO:H_2 = 1:1$ pressure and 100°C [61].

Ethene and propene were removed from refinery dry gases by fixed-bed liquid-phase hydroformylation (50–150°C, 4.8–17.5 bar total pressure) over supported rhodium-based catalyst. The liquid product contained propionaldehyde 86.1%, n-butyraldehyde 4.3%, and 1-propanol 3.6% [62].

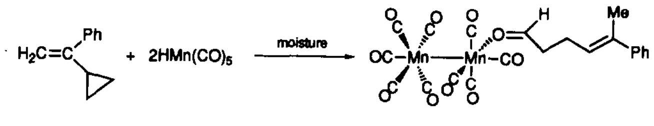
In situ infrared spectroscopic characterization of $HRh(CO)(PPh_3)_3 + PPh_3 + Al_2O_3$ hydroformylation catalyst has shown that the rhodium complex existed as dimer species on the unused catalyst but dissociated to mononuclear complex $HRh(CO)(PPh_3)_2$ in syngas or ethene + CO + H_2 atmosphere under reaction conditions [63].

A dinuclear sulfur-containing rhodium complex immobilized on functionalized diphenylphosphino-(styrene-divinylbenzene) resins catalyzes the hydroformylation of 1-octene at 80°C and 5 bar $CO:H_2 = 1:1$ with 99–100% selectivity in aldehydes and > 90% selectivity in linear aldehyde [64]. Palladium trimethylphosphinecarbonyl clusters encaged in zeolite Y were found to be active in the hydroformylation of propene at 172°C and 20 bar $CO:H_2 = 1:1$ [65]. Up to 96.5% selectivity to n-aldehydes was found in the hydroformylation of 1-pentene at 90°C and 100 bar $CO:H_2 = 1:1$ in the presence of silica supported platinum–tin complexes [66].

2.2. *Coordination chemistry related to hydroformylation*

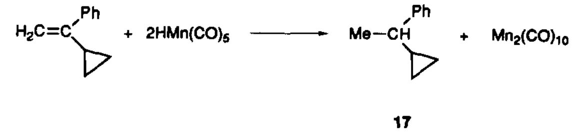
Equilibrium constants for the hydrogenation of $Co_2(CO)_8$ to produce $HCo(CO)_4$ relevant to hydroformylation catalysis in supercritical CO_2 at a gas density of 0.5 g ml^{-1} were determined between 60 and 180°C using *in situ* high pressure ^1H and ^{59}Co NMR spectral measurements. The results for the CO_2 medium are close to reported values for liquid n-heptane solutions [67].

The CO-inhibited stoichiometric reaction of α-cyclopropylstyrene with "wet" $HMn(CO)_5$ gave 70% yield of a ring-opening hydroformylation product **16**.



The manganese alkyl complex $(CO)_5MnCH_2CH_2CH{=}C(Ph)Me$ has been identified as an intermediate in the formation of **16** from α-cyclopropylstyrene and $HMn(CO)_5$.

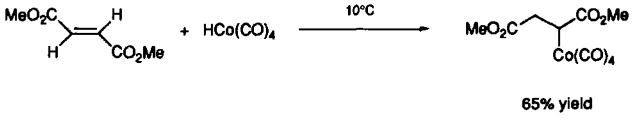
With samples of $HMn(CO)_5$ that have been thoroughly dried and purified using P_2O_5 hydrogenation of α-cyclopropylstyrene to **17** occurred [68].



17

The kinetics and equilibrium of the olefin-promoted interconversion of n-butyryl- and isobutyrylcobalt tetracarbonyl were investigated. The interconversion of n-butyrylcobalt tetracarbonyl and isobutyrylcobalt tetracarbonyl is catalyzed by simple olefins such as ethene, propene, or 1-heptene. The equilibrium constant, $K = [{}^{n}PrC(=O)Co(CO)_4]/[{}^{i}PrC(=O)Co(CO)_4]$ is 1.32 ± 0.03 (25°C), 1.38 ± 0.02 (45°C), 144 ± 0.03 (65°C), and 1.50 ± 0.02 (85°C), which gives $\Delta H = 0.47 \pm 0.2$ kcal mol^{-1} and $\Delta S = 2.13 \pm 0.60$ cal mol^{-1} K^{-1}. The rate of the interconversion is first order with respect to both butyryl complex and olefin and is negative second order with respect to carbon monoxide, and the temperature dependence give $E_a = 41.2 \pm 0.4$ kcal/mol. It was concluded that the aldehyde isomer ratio in the cobalt-catalyzed propene hydroformylation is mainly determined by the rate of this interconversion, which depends dramatically on the partial pressure of carbon monoxide and on the temperature [69].

Tetracarbonylalkylcobalts, supposed intermediates in olefin hydroformylation and aldehyde reduction, were prepared [70]. *E.g.*:



$$OHC\text{-}CHO + HCo(CO)_4 \xrightarrow{-79°C} OHC\text{-}CH(OH)Co(CO)_4$$

2.3. Hydrogenation (reduction) of CO to oxygen-containing organic compounds

The direct ethylene glycol synthesis from carbon monoxide and dihydrogen was studied in the presence of a homogeneous rhodium catalyst combined with a bulky trialkylphosphine such as $^iPr_3P$. High-pressure infrared spectroscopic study showed that $HRh(CO)_3P^iPr_3$ is formed and dinuclear mechanisms in the formation of the intermediate formaldehyde and in the reductive elimination of the hydroxymethyl and the hydroxyacetyl complexes are operating [71].

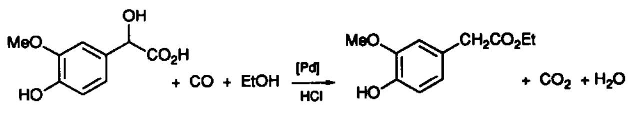
Examples of applications of high-pressure infrared measurements were given among others in the case of the ruthenium–rhodium (10 : 1)-catalyzed ethylene glycol diacetate formation from synthesis gas in glacial acetic acid solution [72].

The mechanism of the homogeneous ruthenium catalyzed ethylene glycol synthesis from carbon monoxide and dihydrogen was studied by high-pressure infrared spectroscopy. It was shown that in the presence of *N*-methylbenzimidazol (L), $Ru(CO)_5$, $Ru(CO)_4L$, and $(LH)^+[Ru_3H(CO)_{11}]^-$ exist at equilibrium in the catalyst solution as major species. The activity in CO hydrogenation was proportional to the concentration of $Ru(CO)_4L$ and a neutral hydride complex, $H_2Ru(CO)_3L$, derived from it, was considered to be the active form. Based on spectroscopic and kinetic results dinuclear mechanisms were found [73].

2.4. Water gas shift reaction and reduction with CO, CO + H_2, or CO + H_2O

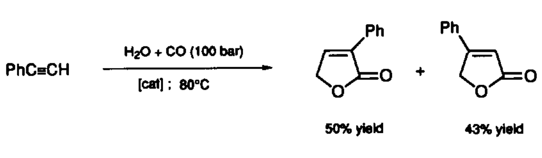
The low temperature water gas shift reaction over $Ru(NH_3)_6Cl_3$, exchanged into the HX and NaX zeolites, was studied by spectroscopic methods [74]. Platinum carbonyl clusters $[Pt_3(CO)_6]_n^{2-}$ ($n = 3, 4$) in NaY zeolite pores were found to be active catalysts for the water gas shift reaction at 27–150°C, and exhibited a marked enhancement of this reaction on illumination with a Xe-lamp [75].

Mandelic acid derivatives, such as α,4-dihydroxy-3-methoxybenzeneacetic acid, were reduced by CO (50 bar) catalyzed by a palladium + HCl system at 110°C in EtOH + benzene = 1/1 (v/v) to the corresponding arylacetic acid derivatives in up to 95% yields [76].



The reaction of 1-butene with carbon monoxide and water in the presence of various bifunctionalized polystyrenes containing diamines, alcohols, and rhodium carbonyl clusters gave at 80°C and 20 bar a mixture of pentanol and 2-methyl-1-butanol in up to 83% yield [77].

Under water–gas reaction conditions terminal acetylenes were selectively converted into furan-2(5*H*)-ones in the presence of $Rh_6(CO)_{16}$ and triethylamine [78]. *E.g.*:



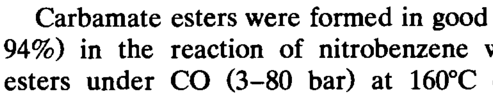
A $Fe(CO)_5$ + sulfur mixture catalyst precursor gave 92.9% coal conversion and 55.8% oil yield in the liquefaction of Yallourn coal heating to 375°C for 60 min and 425°C for 60 min in 1-methylnaphthalene, water, and 70 bar carbon monoxide [79].

The $Pd(OAc)_2 + Et_4NCl + PPh_3$-catalyzed *N,N'*-diphenylurea synthesis from nitrobenzene, aniline and carbon monoxide has been studied at 120°C and 40 bar. By using nitrobenzene-d_5 as a reactant, it was found that *N,N'*-diphenylurea forms via two parallel routes depending on the ratio of aniline to nitrobenzene [80].

$$PhNO_2 + PhNH_2 + 3CO \longrightarrow PhNHCONHPh + 2CO_2$$

$$PhNO_2 + 5PhNH_2 + 3CO \longrightarrow 3PhNHCONHPh + 2H_2O$$

Results of mass spectroscopic analysis of solid products formed at 120°C and 40 bar CO in $Pd(OAc)_2 + PPh_3$-catalyzed reaction of nitrobenzene-d_5, aniline and carbon monoxide suggest that diphenylurea synthesis proceeds through a reaction path involving a carbamoylpalladium intermediate [81]. The reductive carbonylation of nitrobenzene to form methyl-*N*-phenylcarbamate in the presence of methanol in 1,2-dimethoxyethane at 130–170°C and 11–41 bar CO was catalyzed by molybdenum- and vanadium-containing heteropolyanion-modified palladium(II) chloride. A total Pd turnover of 168 was reported [82].



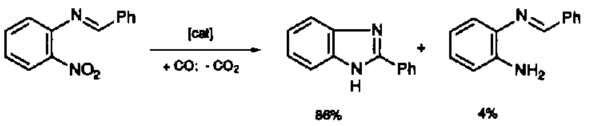
$$PhNO_2 + 3CO + CH_3OH \xrightarrow{[Pd]} PhNH\underset{\underset{O}{\|}}{C}OCH_3 + 2CO_2$$

Carbamate esters were formed in good yields (up to 94%) in the reaction of nitrobenzene with formate esters under CO (3–80 bar) at 160°C catalyzed by $PdCl_2(PPh_3)_2 + O{=}P(^nBu)_3 + KBr$.

$$PhNO_2 + HCOOR + 2CO \xrightarrow{[Pd]} PhNHCOOR + 2CO_2$$

The reaction does not involve the formation of aniline before the carbamate ester formation [83]. Aniline from nitrobenzene and the corresponding amines from aromatic nitro compounds were obtained in > 99% yield using triruthenium-dodecacarbonyl as the catalyst precursor in the presence of triethylamine at 150°C and 20 bar CO [84].

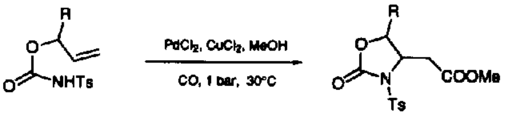
The reaction of **18** with CO at 220°C and 50 bar in benzene in the presence of $Ru_3(CO)_{12}$ as the catalyst gave **19** in good yields [85].



18 **19**

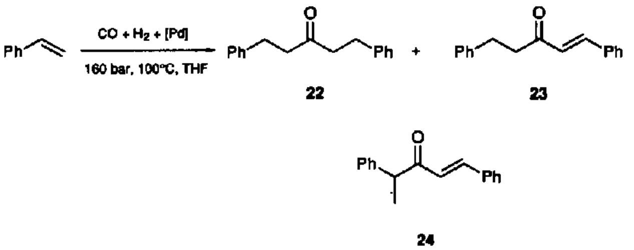
2.5. Hydroformylation-related reactions of CO

Iminodiacetic acid was obtained in 94% optimized yield from acetamide, formaldehyde, carbon monoxide and dihydrogen *via* cobalt-catalyzed amidocarbonylation. Solvent extraction hydrometallurgy was used in recovering cobalt in excellent yield from a water solution containing a strongly chelating amino acid [86]. Carbamates **20** were found to undergo aminocarbonylation to provide **21** by the catalysis of palladium(II) chloride under mild conditions [87].



20 **21**

$[Pd(MeCN)_4][BF_4]_2$ modified with different nitrogen and mono- or bidentate phosphorus ligands was found to catalyze the formation of the ketones **22**, **23** and **24**. *E. g.*: 26 : 66 : 1 and 1.5 : 27 : 69 product selectivities were found in the case of 1,10-phenanthroline and $Ph_2PCH_2CH_2S^cHx$, respectively [88].



22 **23** **24**

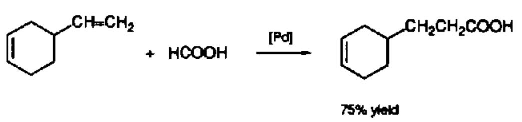
The possible steps of the nickel triad metal-mediated carbalkoxylation of vinyl electrophiles were investigated using platinum complexes as model compounds [89]. A mechanism of the carbalkoxylation of vinyl halides was suggested [90].

The reaction of alkenes with a trialkylsilane and carbon monoxide in the presence of $[IrCl(CO)_3]_n$ or $Ir_4(CO)_{12}$ at 140°C in benzene gave an *E/Z* mixture of 1-silyl enol silyl ethers in 45–85% yields [91].

$$RCH{=}CH_2 + HSiR'_3 + CO \xrightarrow[50\ \text{bar}]{[Ir]} RCH_2CH{=}C(SiR'_3)(OSiR'_3)$$

$(R = Bu, {}^cHx, Me_3C;\ R'_3 = Et_2Me, Et_3, PhMe_2)$

Simple and functionalized olefins were hydrocarboxylated with HCOOH at 150°C under 6.8 bar CO in 1,2-dimethoxyethane solution in the presence of palladium(II) acetate and 1,4-bis(diphenylphosphino)butane as the catalyst precursors [92]. *E. g.*:

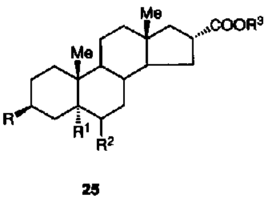


$$OHCC(CH_3)_2CH_2CH{=}CH_2 + HCOOH \xrightarrow{[Pd]} OHCC(CH_3)_2CH_2CH_2CH_2COOH$$

97% yield

Effective reductive carbonylation of methanol to acetaldehyde at 69 bar CO and 140°C in the presence of $Rh(diphosphine)(COMe)(I)_2$ as the catalyst was reported. This catalyst gives rates and selectivities comparable to the best cobalt catalysts (100–200 turnovers per hour, 80–90% yield). Addition of $Me_4NRu(CO)_3I_3$ to this catalyst results in the *in situ* hydrogenation of acetaldehyde and production of ethanol [93]. Basic oxides (MgO, hydroxylated Al_2O_3, and La_2O_3) and acid oxides (*e.g.*: Nb_2O_5) were found to act as heterogeneous promoters for hydrocarbonylation reactions, especially for alcohol homologation, with iodocarbonylruthenium catalysts [94].

Various esters **25** were prepared by hydrocarbonylation of androstene derivatives with alcohols and carbon monoxide catalyzed by a palladium + phosphine catalyst [95].



$R = H; OH$

$R^3 = Me, Et, Pr, CHMe_2, CMe_3$

$R^1 = R^2 = H$
$R^1R^2 = bond$

25

A novel synthesis of lysine, ornithine, and their analogs from the corresponding ω-(phthalimido)alkanals or ω-(phthalimido)alkenes and acetamide in a $Co_2(CO)_8$-catalyzed amidocarbonylation or combined hydroformylation and amidocarbonylation, respectively, at 100°C and 120 bar $CO:H_2 = 1:1$ was reported [96].

2.6. Reduction of CO_2

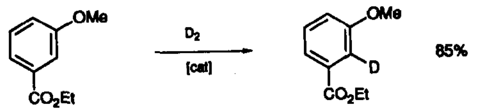
The structure characterization of the key intermediate, $[Ru(bpy)_2(CO)(COO)]$, in a catalytic cycle of the CO_2 reduction has been reported [97]. Formic acid has been produced from dihydrogen and carbon dioxide at room temperature and 40 bar total pressure ($p(H_2) = 20$ bar, $p(CO_2) = 20$ bar) with yields up to 1150 moles per mole of rhodium using *in situ* formed catalyst from $[Rh(COD)Cl]_2$ and dppb in the presence of triethylamine in DMSO solution [98].

Irradiation of $(Me_3P)_4Mo(\eta^2\text{-}CO_2)_2$ in toluene solution at −20°C produced *cis*-$Mo(CO)_2(PMe_3)_4$ and $OPMe_3$ as the major products along with lesser amounts of *mer*- and *fac*-$Mo(CO)_3(PMe_3)_3$ and $Mo(CO)(PMe_3)_5$ [99].

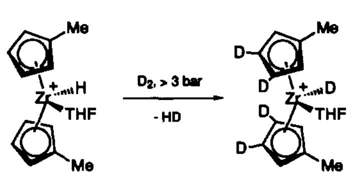
3. Hydrogenation and reduction

3.1. Deuteration and H/D or H/T exchange

The complex $[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$ was found to catalyze the efficient and regioselective exchange of deuterium gas with hydrogens in various aromatic compounds at 25°C and 1 bar. Exchange was observed at sites in proximity to certain nitrogen or oxygen containing functional groups [100]. *E.g.*:



The reaction of **26** with dideuterium results in H/D exchange in the β Cp′ ring positions [101].



26

Tetraallylthorium on dehydroxylated alumina catalyzes the rapid and selective deuteration of linear and cyclic alkanes at 90°C and 3 bar D_2 [102].

See also [108,189,260].

3.2. Hydrogenation of olefins

3.2.1. Fe, Ru, and Os catalysts

K–Na alloy and ferrocene or iron(III) acetylacetonate were used as catalysts for the hydrogenation of dicyclopentadiene, 1-octene, and isoprene at room temperature and atmospheric pressure of dihydrogen [103]. Homogeneous hydrogenation of cyclohexene and 1-hexene catalyzed by (η^6-arene)ruthenium(II) complexes were reported. The monomeric complex $Ru(O_2CMe)_2(\eta^6\text{-}C_6Me_6)$ and $RuCl(O_2CMe)_2(\eta^6\text{-}C_6Me_6)$ in 2-propanol, ethanol or benzene at 50°C and 1 bar H_2 catalyze the hydrogenation more effectively than the derived dinuclear μ-hydrido complexes [104]. Hydrogenation of benzylideneacetone using $OsHCl(CO)(PR_3)_2$ ($PR_3 = P^iPr_3$, PMe^tBu_2) as the catalyst precursor gave selectively 4-phenylbutan-2-one [105].

The kinetics of hydrogenation of *cis*-1,4-polybutadiene in the presence of $RuCl(CO)(OCOPh)(PPh_3)_2$ as catalyst at 85°C and 1 bar H_2 were found to be first order with respect to [Ru], [C=C], and $[H_2]$, and negative first order with respect to $[PPh_3]$ [106].

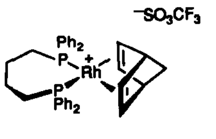
See also [194].

3.2.2. Co, Rh, and Ir catalysts

The catalytic activity of phosphido-bridged dirhodium complexes having a μ-Cl ligand was studied in some hydrogen transfer processes, Thus, *cis*-$[R_2R'PRh(CO)]_2(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)$ ($R = R' = {}^tBu$; R = Ph, R′ = 5β-methyl-2α-(1α-methylethyl)cyclohexyl) was found to be highly active catalysts for hydrogenation of styrene and (*Z*)-methyl α-acetamidocinnamate and for hydroformylation of cyclohexene. The chiral complex, in which the tri-tert-butylphosphine groups have been replaced by (+)-neomenthyl-diphenylphosphine ligands, promotes enantioselective hydrogenation of (*Z*)-methyl α-acetamidocinnamate at 70°C and 35 bar H_2 [107].

Diastereoselective hydrogenation (deuteration) of monodehydro enkephalins were performed using RhCl(DIOP), RhCl(BPPM), and $[Rh(DIPAMP)(COD)]^+BF_4^-$ as the catalyst. DIPAMP was found to be the most effective ligand [108].

Hydrogenation of vinyl sulfoxides and vinyl sulfones were studied using cationic rhodium complexes **27** and **28** as the catalysts at 25°C and 1–1.5 bar H_2 [109].



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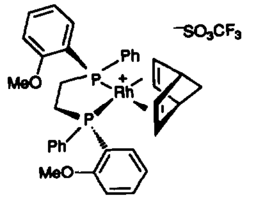

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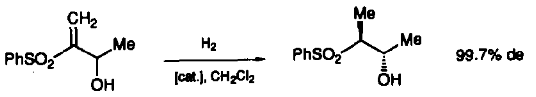
E.g.:



The catalytic hydrogenation of cinnamic acid at 30°C and 1 bar pressure of dihydrogen in the presence of dihydro(1,3-diphenyltriazenido)bis(triphenyl-phosphino)rhodium(III) was studied. The catalytic activity decreased in the order:

DMSO $\gg$ DMF $>$ acetone $\approx$ benzene $>$ toluene $>$ THF [110].

Hydrogenation of 1-hexene using $[Rh_6(CO)_{15}(SMe_2)]$ as a catalyst precursor was observed at 60°C with a highest rate of 2200 turnovers/h [111]. The dicarbonyl (2,4-pentadionato)rhodium complex was found to be an efficient catalyst of hydrogenation and hydrosilylation of 1-octene [112]. The selective catalytic hydrogenations of the C=C double bond in acrylonitrile, acrolein, and acrylic acid at 30°C and atmospheric pressure using $RhH_2(Ph_2N_3)(PPh_3)_2$ in THF were reported. The effect of variables was investigated [113].

Kinetic analysis and mechanistic studies have been made on the hydrogenation of styrene-butadiene copolymers in the presence of $RhCl(PPh_3)_3$ as the catalyst [114]. The kinetics of hydrogenation of cyclohexene using heterogenized $RhCl(PPh_3)_3$ on montmorillonite were studied in the temperature range of 10–40°C [115].

Kinetic evidence for the participation of an $Ir(\eta^2\text{-}H_2)$ complex in the hydrogenation of benzylideneacetone to 4-phenylbutan-2-one catalyzed by $IrClH_2(P^iPr_3)_2$ has been found [116]. The catalytic activity of $IrCl(CO)(PPh_3)_2$ for propene hydrogenation showed a maximum when a porous silica catalyst support with cavities of > 100 Å was applied [117].

See also [125,238].

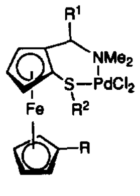
3.2.3. *Ni, Pd, and Pt catalysts*

The catalytic activity of nickel phthalocyanine absorbed in NaY zeolite was studied in liquid-phase hydrogenation of cyclohexene [118].

Hydrogenation catalysts based on palladium(II)-poly(vinylpyridine) complexes were found to be active for allyl alcohol hydrogenation in aqueous solution at 25°C and 1 bar dihydrogen pressure. Maximum hydrogenation activity was obtained at ligand : Pd: ratio of 1 : 1 [119]. A preferential substrate selectivity in hydrogenation of olefins at 1 bar and room temperature by montmorillonite diphenylphosphine palladium(II) chloride catalyst was reported. In competitive hydrogenation reaction a 1 : 1 molar mixture of methyl acrylate and n-octyl acrylate gave methyl propionate in 95% selectivity at 1 equiv. absorption of dihydrogen [120].

The palladium cluster $[Pd_5P_4Ph_6]$, obtained from $Pd(acac)_2PPh_3$ with H_2 in DMF at 30–80°C, was found to catalyze the hydrogenation of unsaturated hydrocarbons [121].

Complexes **29** were applied as catalysts for the hydrogenation of double and triple bonds conjugated to functional groups and aromatic systems at room temperature at 5 bar [122].



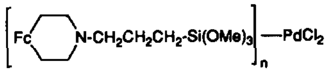
R = H, SMe, S-4-tolyl

R^1 = H, Me

R^2 = Me, 4-tolyl

29

Bimetallic catalysts **30** immobilized on silica supports were tested for their catalytic activity for hydrogenation of styrene, nitrobenzene, cyclohexene, acrolein, acrylic acid, 1-decene, and α-pinene. The initial hydrogenation rate increased with N/Pd ratio and the catalytic activity of **30** was much higher than that of monometallic analogs [123].



Fc = ferrocene

n = 1, 2, 4, 6

30

The hydrogenation of nitrile rubber using a palladium acetate homogeneous catalyst system was investigated. The effect of different reaction parameters on the degree of hydrogenation was studied [124]. Hydrogenation of liquid carboxylated nitrile rubber was carried out using homogeneous palladium and rhodium catalysts. The palladium complex of 2-benzoylpyridine was found to be a selective catalyst for the reduction of the carbon–carbon double bonds without affecting the nitrile and carboxyl functionality. A great extent of decarboxylation was obtained for samples hydrogenated in the presence of a rhodium complex [125].

See also [200].

3.2.4. *Other metals as catalysts*

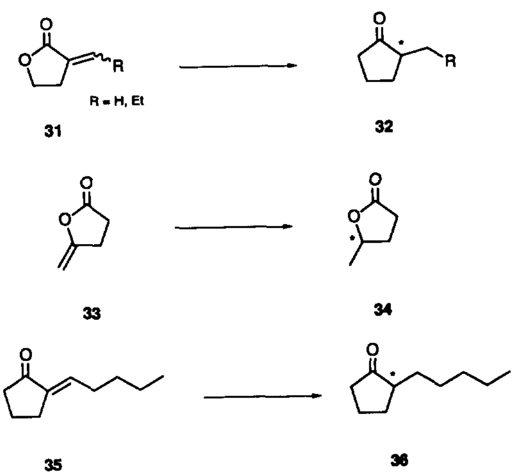
The titanocene complex with tolane was found to catalyze the homogeneous hydrogenation of olefins and acetylenes at room temperature and atmospheric pressure [126].

See also [182].

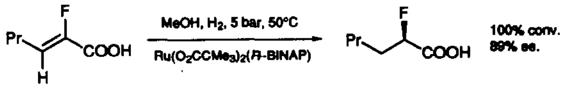
3.3. Asymmetric hydrogenation of prochiral compounds

3.3.1. Asymmetric hydrogenation of olefins

The asymmetric hydrogenation of tiglic and angelic acids was studied at different dihydrogen pressures using chiral ruthenium(II) bisphosphine catalysts [127]. Asymmetric hydrogenation of **31**, **33**, and **35** at 50°C under 100 bar of H_2 in CH_2Cl_2 catalyzed by Ru $(OAc)_2$(BINAP) complex afforded **32**, **34**, and **36**, respectively in 94–98% ee [128].

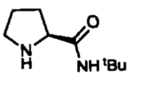


Asymmetric hydrogenation of 2-fluoro-2-alkenoic acids catalyzed by ruthenium–BINAP complexes at 5 bar dihydrogen pressure and 50°C afforded optically active 2-fluoroalkanoic acids in up to 90% ee [129]. *E.g.*:



A practical synthesis of BINAP–ruthenium(II) dicarboxylate complexes was reported. Hydrogenation of α,β-unsaturated carboxylic acids was found to be faster with the dicarboxylate complex than with the corresponding dichloro complex [130]. The asymmetric hydrogenation of itaconic acid and other prochiral carboxylic acids under mild conditions have been studied using $[RuH(BINAP)_2]PF_6$ as catalyst precursor. The addition of triethylamine effected > 90% enantioselectivities. ^1H and ^{31}P NMR examinations of the reaction mixtures revealed ruthenium species containing one BINAP chelate [132].

Optically active complexes of Rh, Ru, Co, and Ni having **37** or **38** ligands were tested for hydrogenation of ethyl α-benzoylaminocinnamate at 65°C under 5 bar dihydrogen. The corresponding substituted phenylalanine derivative was obtained with quantitative conversions and high enantioselectivity. Zeolite-supported complexes show a higher activity and produce a remarkable increase of enantioselectivity > 95% [132].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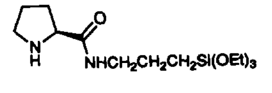
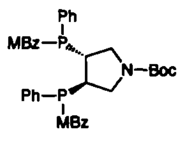

38

Various activated and inactivated olefins were hydrogenated using *cis*-$[MH_2(dcpe)_2]$ (M = Ru, Os; dcpe = 1,2-bis(dicyclohexylphosphino)ethane) as the catalyst precursor at 100°C and 20 bar dihydrogen. The ruthenium catalyst was found to be more active for the reduction of enones to saturated ketones than for the reduction of inactivated olefins. In contrast, the hydrogenation of inactivated olefins was found to be faster in the presence of the osmium catalyst [133].

The effect of *N*-substituent on the enantioselectivity and the catalytic activity of the rhodium complex of pyrrolidinebisphosphine ligand was examined by means of hydrogenation studies with 2-methylene succinamic acid and phenylacylamine derivatives and ^{31}P spectral analysis [134]. The influence of β-arranged substituents in chiral seven-membered rhodium diphosphine rings on asymmetric hydrogenation of (*Z*)-α-acetamidocinnamic acid was investigated [135]. The rate of catalytic asymmetric hydrogenation of ethyl (*Z*)-α-acetamidocinnamate in the presence of [Rh(NBD)(CHIRAPHOS)]BF_4 as the catalyst was estimated spectroscopically through enhanced resonances using parahydrogen [136].

Racemic α-(α-aminoalkyl)acrylates were hydrogenated using a variety of Rh^I cationic complexes containing diphosphines and $Ru(OAc)_2$(*S*)-BINAP as catalyst precursors to give preferentially the *threo* isomers [137].

Cationic rhodium complexes with the new 1,2-bisphosphines **39-41** were tested as catalysts in enantioselective hydrogenation of acetamidocinnamic acid in methanol at 25°C and between 1 and 75 bar dihydrogen pressures. Quantitative yields and the formation of the *S*-isomer in up to 92% ee were reported [138].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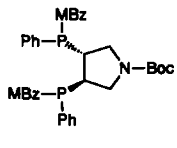
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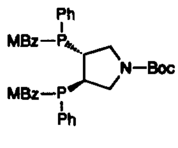
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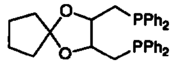
(MBz = 2-methoxybenzyl; Boc = *tert*-butoxycarbonyl)

(*S*)-(−)-2-Methyl succinamic acid was prepared by homogeneous asymmetric hydrogenation of 2-methylenesuccinamic acid catalyzed by (2*S*,4*S*)-*N*-substituted-4-(diphenylphosphino)-2-[(diphenylphosphino)-methyl]-pyrrolidine-rhodium complexes [139]. DIOP-type chiral ligands such as **42** were used in rhodium-catalyzed enantioselective hydrogenation of α-acetamino cinnamic acid. Alanine was obtained in 76–82% ee [140]. Up to 70% optical purity of (*S*)-*N*-acetylphenylalanine has been obtained in asymmetric hydrogenation of (*Z*)-α-acetamidocinnamic acid using various rhodium(I) complexes with (*R*,*R*)-DIPPOP (**43**) as the catalysts at 25°C and 3 bar dihydrogen [141].



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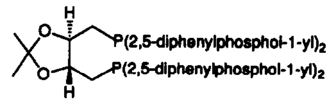
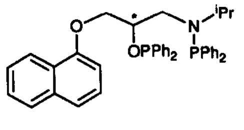


43

(*Z*)-α-N-benzoylamino-β-(fluorophenyl)acrylic acids and their esters were hydrogenated to the corresponding optically active α-benzoyl-β-(fluorophenyl)-alanine derivatives with optical yields up to 90% using rhodium complexes of **44** and **45** as chiral catalysts [142].



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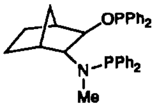
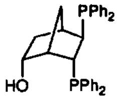


45

The new ligand **46** was tested in asymmetric hydrogenation of (*Z*)-*N*-acetyl dehydrophenylalanine under 1 bar dihydrogen in form of an *in situ* complex with [RhCl(COD)]₂ as catalyst in ethanol. In comparison with NORPHOS (*47*), the new ligand gave a much more active catalyst, leading to (*S*)-*N*-acetylphenylalanine with 98% ee [143].



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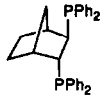
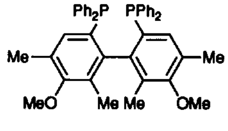


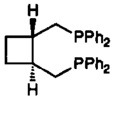
47

Rhodium(I) complex of optically pure atropisomeric **48** showed higher catalytic activity and better enatioselectivity with the reverse configuration than BIMOP, *p*-MeO-BIMOP, and BINAP in the asymmetric hydrogenation of (*Z*)-α-acetamidocinnamic acid, itaconic acid, and its derivatives [144].



48

The hydrogenation of dehydropeptides in a two-phase system using [Rh(COD)Cl]₂ with chiral water-soluble ligands derived from CYCLOBUTANEDIOP (**49**) and BDPP (**50**) was studied. Diastereoselectivities of up to 87% were obtained with tetrasulfonated BDPP [145].



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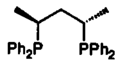
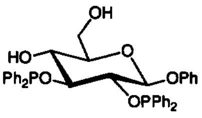


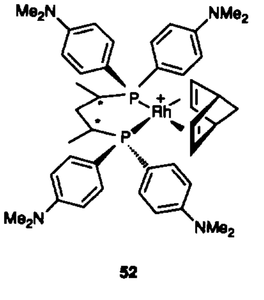
50

Increase in catalytic activity and enantioselectivity in asymmetric hydrogenation reactions catalyzed by chiral rhodium(I) complexes in the presence of micelle-forming amphiles was reported. In a typical experiment, 15 mmol of (*Z*)-methyl 4-acetoxy-3-methoxy-α-acetamidocinnamate were suspended in the presence of 0.17 mmol sodium dodecylsulfate and 0.03 mmol [Rh (COD)(Ph-β-glup-OH)]BF₄ (Ph-β-glup-OH = **51**) in 50 ml water, giving 100% conversion, 90% ee, after 5h hydrogenation at 60°C and 1 bar dihydrogen [146].



51

Immobilization of **52** and **53** on a soluble form of the strongly acidic Nafion-H cation exchange resin resulted in catalytic asymmetric hydrogenation activities that approach those of their homogeneous counterpart in asymmetric hydrogenation of α-acylaminocinnamic acid and its methyl ester [147].



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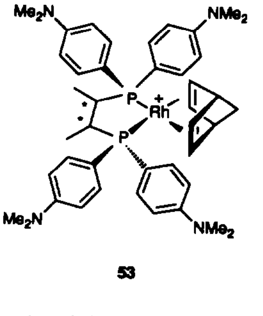


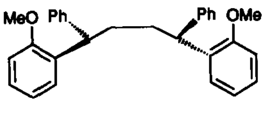
53

Chiral diphosphines, obtained in kinetic resolution of the racemic mixture with configurationally pure bis(menthyl-(*Z*)-α-acetamidocinnamate)iridium tetrafluoroborate, combined with bis(norbornadiene)rhodium tetrafluoroborate gave active enantioselective hydrogenation catalysts for the hydrogenation of methyl (*Z*)-α-benzamidocinnamate [148,149]. Asymmetric hydrogenation of unfunctionalized olefins with high turnover frequencies and enantioselectivities was reported using chiral organosamarium complexes. Kinetic measurements yielded the rate law: $v = k[\mathrm{Sm}]^{1/2}[\mathrm{H_2}][\text{2-Ph-1-butene}]^0$ [150].

See also [107,151,157,159].

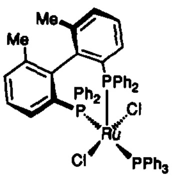
3.3.2. Asymmetric hydrogenation of ketones

Ruthenium (*R*,*R*)-DIPAMP complexes (were found ((*R*,*R*)-DIPAMP = **54**) were found to be effective for asymmetric hydrogenation of both olefins and keto groups (35–80% ee) [151].



54

The ruthenium complex **55** was found to be a very active and enantioselective catalyst for the mono- and dihydrogenation of 2,4-pentanedione at 50°C and 100 bar of dihydrogen. High yields and > 99% ee of the *S* or *S*,*S* products were reported. Complex **55** displays catalytic activity also under hydrogen transfer conditions, in refluxing isopropanol under argon [152].



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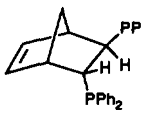
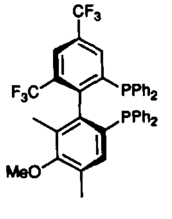


56

The neutral rhodium catalyst prepared *in situ* from bis(2,5-norbornadiene rhodium chloride) and NORPHOS (**56**) was found to be an excellent catalyst for enantioselective hydrogenation of aliphatic α-keto esters to the corresponding α-hydroxy esters. The reaction parameters for the hydrogenation of ethyl 2-oxo-4-phenylbutyrate were optimized, and the best optical yields obtained were 96% [153].

The relationship between the structure of various $\mathrm{Ru^{II}}$(BINAP) complexes and their catalytic activities for asymmetric hydrogenation was investigated [154].

The FUMOP-ruthenium(II) complex ((*S*)-(–)-FUMOP = **57**) was found to be an excellent catalyst for the asymmetric hydrogenation of methyl 3-oxobutanoate to (*S*)-methyl 3-hydroxybutanoate at 30–40°C and 10–30 bar dihydrogen. High chemical yield and very high enantioselectivity (> 99% ee) was achieved [155]. The asymmetric hydrogenation of β-keto esters such as tert-butyl acetoacetate in methanol at 40°C and 2 bar dihydrogen in the presence of 0.1 mol% of HCl and 0.02–0.05 mol% $[(R)\text{-Ru(BINAP)Cl}_2]_2 \cdot \mathrm{NEt_3}$ gave the corresponding alcohol in 97 + % ee [156]. Asymmetric hydrogenation of prochiral α,β-unsaturated carboxylic acids using $\mathrm{RuCl_2(ArCN)_2(BINAP)}$ and $\mathrm{Ru_2Cl_2(BINAP)_2(NEt_3)}$ complexes (ArCN = benzonitrile, 2-furancarbonitrile, pentafluorobenzonitrile) as the catalysts were studied. 100% yields and 98% ee were obtained in hydrogenation of methyl 3-oxo-butyrate and 4-hydroxy-2-butanone in the presence of $\mathrm{Ru_2Cl_2(BINAP)_2(NEt_3)}$ at 35°C and 100 bar H_2 in methanol [157]. Ion-pairing of anionic carbonyl clusters of platinum and ruthenium with cinchona alkaloid groups on cross-linked polystyrene resulted in useful catalysts for the asymmetric hydrogenation of α-ketoesters [158]. An *in situ* prepared rhodium(I) complex with a new atropisomeric biphenylbisphosphine **58** was found to be an efficient catalyst in the asymmetric hydrogenations of **59** and **60** at 50°C and 90 bar, and at 30°C and 5 bar, respectively [159].



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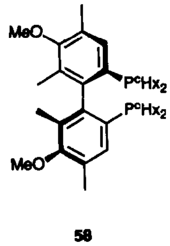

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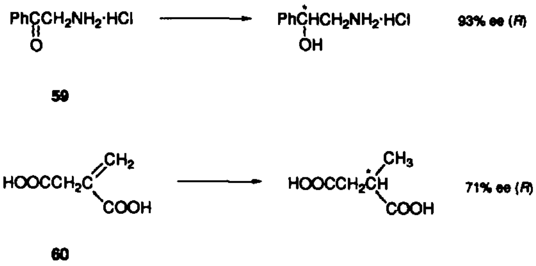
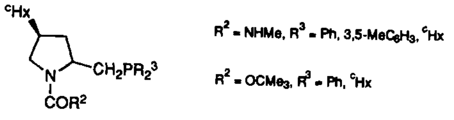


Asymmetric hydrogenation of $\mathrm{PhCOCH_2CH_2NRR^1}$ (R = $\mathrm{CH_2Ph}$, H; $\mathrm{R^1}$ = Me in the presence of [Rh $\mathrm{(COD)Cl]_2}$-(2*S*,4*S*)-**61** gave $\mathrm{PhCH(OH)CH_2CH_2NRR^1}$ with *R*-configuration at the hydroxy carbon [160].



61

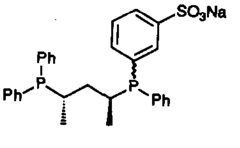
Asymmetric hydrogenation of α,β-unsaturated carbonyl compounds to allylic alcohols catalyzed by [Ir(BINAP)(COD)]BF_4 + *o*-dimethylaminophenyldiphenylphosphine was studied. Thus (*E*)-4-phenyl-3-buten-2-one afforded (*E*)-4-phenyl-3-buten-2-ol in 97% chemoselectivity and in 65% enantiomeric excess. A mixed ligand iridium dihydride complex containing both BINAP and the aminophosphine ligand was shown to be the catalytically active species [161]. Simple cyclic enones such as 2-cyclohexen-1-one were selectively hydrogenated to the corresponding allylic alcohols in the presence of an *in situ* catalyst formed by $[Ir(COD)(OMe)]_2$ and DIOP. Optical purities up to 28% were achieved [162].

3.3.3. Asymmetric hydrogenation of imines and oximes

An asymmetric titanocene-catalyzed hydrogenation of ketimines at 65°C and under 140 bar dihydrogen pressure gave enantioenriched amines in high yield and high ee [163]. *E.g.*:

77% yield, 98% ee

The ruthenium BINAP complex, [RuCl(benzene)(*R*)-BINAP]Cl, was found to catalyze the asymmetric hydrogenation of oximes to amines in moderate enantiomeric excess [164]. The enantioselectivity in the rhodium-catalyzed acetophenone N-benzylamine hydrogenation at 20°C and 70 bar dihydrogen was improved dramatically by using a mono-sulfonated BDPP ligand **62** (94% ee) instead of the unsulfonated (65% ee) or the disulfonated one **63** (2% ee) [165].



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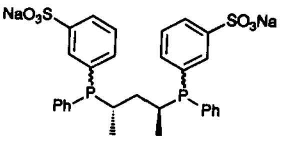
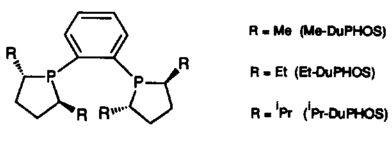


63

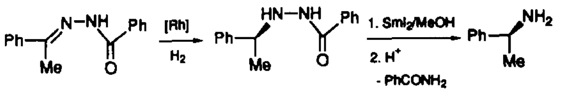
Using immobilized rhodium(I)-diphosphine catalysts supported on silica gel, the C=N bonds of the pyrazine ring of folic acid were reduced with 40 bar dihydrogen at 80°C in aqueous solution to give 5,6,7,8-tetrahydrofolic acid. By using optically active chelate phosphines as co-catalysts, a diastereomeric excess of up to 24% of the natural isomer was achieved [166].

A homochiral series of 1,2-bis(phospholano)benzenes **64** have been tested in the rhodium-catalyzed asymmetric hydrogenation of the C=N group of *N*-acylhydrazones.



64

Et-DuPHOS proved to be superior in terms of enantioselectivity. *E.g.*: hydrogenation of the *N*-benzoylhydrazone of acetophenone at 20°C and 1 bar H_2 using 0.1 mol% $[(COD)Rh(Et\text{-}DuPHOS)]^+CF_3SO_3^-$ as catalyst precursor provided the product *N*-benzoylhydrazine in 88% ee. The *N*-benzoylhydrazine was transformed into the corresponding amine with no loss of optical purity using ≥ equiv. of SmI_2 [167].



3.4. Hydrogenation of dienes and alkynes

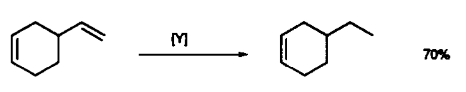
The effect of temperature, solvent and the amount of catalyst in the catalytic hydrogenation of diphenylacetylene using the $Cp_2TiCl_2 + Me_2CHMgBr$ system was investigated [168].

Surface compounds formed in the reaction of $Co_2(CO)_8$ with laminar disulfides MS_2 (M = Ti, Mo) were found to catalyze the hydrogenation of butadiene to give 1-butene as the major product [169]. Tricarbonylchromium(0) species encaged in LiX or NaX zeolite were found to be highly efficient and stereo selective for the hydrogenation of butadiene at −43°C to *cis*-2-butene and 1-butene [170]. The hydrogenation of conjugated dienes $R(CH{=}CH)_2R'$ having an oxygen function in R′ (*e.g.*; R′ = CO_2Me, CMe_2OH, CH_2OAc, COMe) gave in the presence of $Cr(CO)_6$ as the catalyst at 160–180°C under 50–80 bar dihydrogen in hexane solution the corresponding *cis*-alkenes in ≤ 99% yield [171]. The kinetics of the homogeneous 1,4-hydrogenation of conjugated dienes (*e.g.*: methyl sorbate) catalyzed by (naphthalene)$Cr(CO)_3$ in polar coordinating solvents at 1 bar H_2 and room temperature were investigated. The rate of hydrogenation is first order in catalyst, diene, and H_2 at low concentrations. Fractional orders were obtained at higher concentrations [172].

Selective catalytic hydrogenation of 1-alkynes to alkanes was observed between 20 and 63°C at 1 bar H_2 pressure in THF solution in the presence of $[\{P(CH_2CH_2PPh_2)_3\}_3Fe(H)(H_2)]BPh_4$. A kinetic study on the hydrogenation of PhC≡CH to PhCH=CH$_2$ has shown that the reduction is first order in catalyst and alkyne concentrations and zero order in H_2 pressure [173]. The trinuclear complex $[Ru_3(\mu\text{-}H)(\mu\text{-}C_8H_{11}N_2)(CO)_9]$ ($C_8H_{11}N_2$ = 1,2-diamino-4,5-dimethylbenzene) was found to be a catalyst precursor for the selective homogeneous hydrogenation of diphenylacetylene to stilbene at 60°C and 1 bar H_2. Kinetic and chemical evidence suggest that mononuclear complexes are the catalytically active species [174]. A layer-segregated platinum-ruthenium cluster complex, $Pt_3Ru_3(CO)_{20}(\mu_3\text{-}PhC_2Ph)(H)_2$, was found to exhibit high activity for the selective catalytic hydrogenation of diphenylacetylene to (*Z*)-stilbene in hexane solution at 50°C and 1 bar H_2 [175]. The catalytic activity of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ampy)(CO)_9]$ (Hampy = 2-amino-6-methylpyridine) in the hydrogenation of alkynes and alkenes under homogeneous conditions was reported [176]. The *cis*-hydrido(η^2-dihydrogen)ruthenium(II) complex with $P(CH_2CH_2PPh_2)_3$ ligand was found to be an active catalyst precursor for the selective hydrogenation of phenylacetylene to styrene. The rate of the catalytic hydrogenation reaction is proportional to the initial concentration of the catalyst precursor, second order with respect to dihydrogen pressure, and independent of substrate concentration [177].

Hydrogenation of 3,8-nonadienoic acid with $RhCl[P(p\text{-tolyl})_3]_3$ in benzene at 1 bar and 30°C gave mainly 3-nonenoic acid, whereas the addition of water changed the selectivity in favor of 8-nonenoic acid [178]. Palladium complexes of achiral and chiral ferrocenylamine sulfides were tested as catalysts in hydrogenation of 1,3-cyclooctadiene. The effects of pressure on the reaction rates and selectivities were investigated [179].

Substituted dienes with isolated double bonds were selectively hydrogenated to the corresponding monoene at room temperature and 1 bar H_2 using $Cp^*)_2YMe(THF)$ as the catalyst precursor [180]. *E.g.*:



Silica-immobilized lanthanides, having the structure ≡Si–O–M–NH$_2$ (M = Eu, Yb), showed selective hydrogenation properties, discriminating between conjugated and non conjugated dienes [181].

See also [103,126,182].

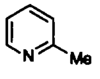
3.5. Hydrogenation of arenes and heterocyclic compounds

The hydrogenation of various linear and cyclic mono- and di-olefins and aromatic substrates have been investigated using $[Cp_2ZrH(CH_2PPh_2)]_n$ as the catalyst. Selective formation of cycloheptene, cyclooctene and 1,2,3,4-tetrahydroanthracene was obtained from cycloheptatriene, cyclooctadiene (1,3 or 1,5) and anthracene, respectively, at 80°C and 40 bar dihydrogen. Based on kinetic results a homobimetallic $Zr^{IV}Zr^{II}$ complex was suggested as the active species. A mechanism for the hydrogenation of conjugated diolefins was postulated [182].

Catalytic hydrogenation of a wide variety of aryl phosphines by niobium aryloxide compounds at 80°C and 80 bar dihydrogen in cyclohexene solution gave high yield of the corresponding cyclohexyl phosphines [183]. The niobium tris(4-methylbenzyl) compound $Nb(OC_6H_3Ph_2\text{-}2,6)_2(CH_2C_6H_4\text{-}4Me)_3$ was found to act as a catalyst precursor for the hydrogenation of benzene and a variety of polynuclear aromatic hydrocarbons at 80°C and 80 bar. The tantalum trihydride compound $Ta(OC_6H_3^cHx_2\text{-}2,6)(H)_3(PMe_2Ph)_2$ was also active in hydrogenation of naphthalene and anthracene in cyclohexane solution. The stereochemistry of the hydrogenations have been studied by using perdeuterated arenes [184].

Potential advantages (*e.g.*: solubility in polar solvents) of heteropolyanions $[PM_{12}O_{40}]^{4-}$ (M = Mo or W) over conventional catalysts for quinoline hydrogenation were discussed [185]. The kinetics of hydrogenation of benzene in the presence of $\eta^3\text{-}C_3H_5\text{-}Co[P(O\text{-}^iPr)_3]_3$ as the catalyst precursor were investigated [186].

The complex $[Rh(COD)(Ph_2PCH_2COO)]$ and $[Rh(CO)_2(Ph_2PCH_2COO)]$ show catalytic hydrogenation activities towards benzene and a variety of substituted benzenes at 50°C and 5 bar dihydrogen [187]. Five- and six-membered aromatic ring N compounds and five-membered aromatic ring S and O compounds (**65–73**) were regioselectively hydrogenated in the heteroaromatic ring at 40°C and 30 bar dihydrogen with $[Cp^*)Rh(MeCN)_3]^{2+}$ as the catalyst precursor.



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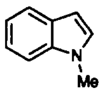

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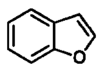

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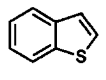

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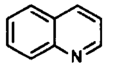

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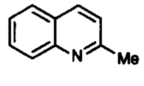

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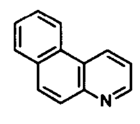

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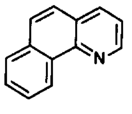

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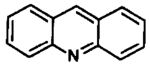


73

The order of relative rates as a function of structure was found to be **72** ⋙ **73** > **69** > **71** > **70** > **68** ≫ **65–67** [188]. Room-temperature catalytic hydrogenation of benzene and toluene at atmospheric pressure was achieved by using $[(COD)RhH]_4$ as a catalyst precursor. Under similar conditions pyridine-d_5 underwent *ortho* D/H exchange [189]. The conversion of chlorobenzene, 1,2,4-trichlorobenzene and 1-chloronaphthalene into the corresponding saturated hydrocarbons is catalyzed by a homogeneous rhodium catalyst generated from $[(C_5Me_5)RhCl_2]_2$ in the presence of excess NEt_3 under 40 bar dihydrogen at 75°C [190].

Aniline, phenol, and benzoic acid were hydrogenated to cyclohexylamine, cyclohexanol, and cyclohexanecarboxylic acid in about 100% yield without any byproduct at room temperature and 1 bar dihydrogen pressure in the presence of a new polymer-platinum complex of starch-poly-γ-aminopropylsiloxane as the catalyst [191]. Thorium complex, $Th(\eta^3\text{-allyl})_4$ supported on dehydroxylated γ-alumina was found to be a highly active catalyst for benzene hydrogenation at 90°C and 12 bar dihydrogen. The kinetics and mechanism of the reaction were studied [192].

3.6. *Hydrogenation of carbonyl compounds*

The kinetics of the homogeneous catalytic hydrogenation of benzaldehyde in 2-methoxyethanol in the presence of $[RuH(CO)(NCMe)_2(PPh_3)_2][BF_4]$ as the catalyst were investigated [193]. *cis*-$[Ru(6,6'\text{-}Cl_2bpy)_2(OH_2)_2][CF_3SO_3]_2$ was found to be an active hydrogenation catalyst at 105°C and 40 bar dihydrogen for carbonyl compounds (aldehydes and ketones) and olefins [194]. Cyclic esters like γ-butyrolactone were catalytically hydrogenated at 200°C and 50 bar dihydrogen in the presence of a series of ruthenium complexes with triphenylphosphine ligands to afford the corresponding α,ω-diols with high selectivity [195]. Water-soluble ruthenium complexes with the $P(C_6H_4\text{-}m\text{-}SO_3Na)_3 \cdot 3H_2O$ ligand have been tested in the catalytic hydrogenation of propionaldehyde in water at 100°C. Addition of alkaline, alkaline-earth and ammonium salts dramatically increased the activity of the catalyst [196].

Selective catalytic hydrogenation of α,β-unsaturated aldehydes and ketones was observed using $Os_3(CO)_{12}$ and phosphines as the catalyst precursors at 140°C and 45 bar dihydrogen. For example, the hydrogenation of crotonaldehyde with $P^nBu_3 + Os_3(CO)_{12}$ (15/1) afforded 89% yield of crotylalcohol at 93% conversion [197]. The complex $[Rh(NBD)(PMe_2Ph)]BF_4$ was found to be a precatalyst for the hydrogenation of carbon dioxide to formic acid at 40°C and 100 bar $CO_2/H_2 = 1$ [199].

The hydrogenation of 3-(2-furyl)acrolein to the corresponding saturated aldehyde and alcohol was studied using $Pd(FZ)_2Cl_2$ (FZ = 1-[(5-nitrofurfurylideneamino)-1,3,4-triazole]) as catalyst in the presence and absence of additives ($NaBH_4$, CCl_4, Zn compounds) [200].

See also [48,93,203,207].

3.7. *Hydrogenation of nitro compounds*

In the presence of methyl formate, tetrabutylphosphonium bromide and catalytic amounts of $Ru_3(CO)_{12}$, nitroarenes were selectively converted into *N,N*-dimethylaminoarenes at 220°C. Methyl formate is the source of hydrogen for reducing the nitrocompounds and serves as methylating agent [201].

Polymer-anchored Ru^{III} complexes were tested in the hydrogenation of nitrobenzene in the temperature range 30–50°C. The catalytic activities of the polymer-bound catalysts were found to be higher than those of their homogeneous counterparts [202]. Nickel(I) complexes with polymer ligands containing oxygen, nitrogen and sulfur atoms were used as catalyst precursors in hydrogenation of nitro compounds, aldehydes and ketones [203].

See also [123,207].

3.8. *Miscellaneous hydrogenations*

Silica-gel-supported zirconium hydride $[(\equiv SiO)_3ZrH]$ was found to be an effective hydrogenolysis catalyst for alkanes such as neopentane, isobutane, and propane, affording ethane and methane as final products at 50°C [204].

Di- and trinuclear ruthenium(II) complexes combined with $Ph_2P(CH_2)_4PPh_2$ were found to catalyze the homogeneous hydrogenation of benzonitrile to benzylamine, the imine $PhCH_2N{=}CHPh$, or dibenzylamine, depending on reaction conditions [205].

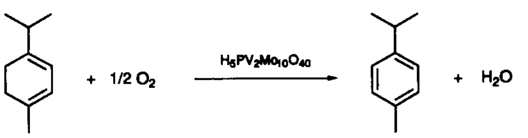
$[Ir_6(CO)_{15}]^{2-}$ in NaX zeolite was found to catalyze CO hydrogenation at 1 bar and 175°C giving high yields of C_1–C_5 alkanes and alkenes [206].

Dinuclear orthometalated Schiff base complexes of palladium(II) were found to be efficient hydrogenation catalysts of organic NO_2, C=O, C=N, N=N, and C≡N groups under normal or high pressure conditions [207].

3.9. *Dehydrogenation*

Dehydrocoupling of ammonia and Ph_2MeSiH or $PhMeSiH_2$ to give the corresponding disilazanes $Ph_2MeSiNHSiPh_2Me$ or PhMeHSiNHSiHPhMe, respectively, was effectively catalyzed by dimethyltitanocene [208]. Dehydrogenative polymerization of methylsilanes using Cp_2MMe_2 (M = Ti, Zr) as the catalyst afforded mixtures of oligosilanes and a polysilane [209].

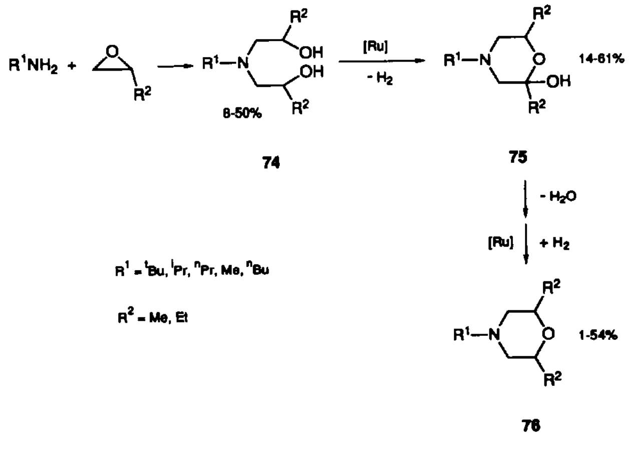
The kinetics and mechanism of the aerobic oxidative dehydrogenation of α-terpinene to p-cymene catalyzed by the mixed heteropolyanion $PV_2Mo_{10}O_{40}^{5-}$ were investigated. The reaction is zero order in α-terpinene, first order in dioxygen, and second order in the heteropolyanion catalyst [210].



The heteropoly complex of ammonium lanthanum tungstate, $(NH_4)_7[LaW_{10}O_{35}]_2O$ showed some catalytic activity in dehydrogenation of isopropanol to acetone [211].

High molecular weight poly(methylsilylene) was obtained in good yield through dehydrogenative condensation of methylsilane catalyzed by $(C_5Me_5)_2NdCH(SiMe_3)_2$ [212].

The reaction of primary amines with epoxides in the presence of tributylphosphine, ruthenium trichloride hydrate and p-dioxane afforded at 180–220°C various yields of **74**, **75** and **76** depending on the substituent and the temperature [213].



$RhCl(PMe_3)_2(CO)$ was found to catalyze the highly efficient thermal transfer-dehydrogenation of alkanes (*e.g.*: cyclohexane, n-hexane) to alkenes under 70 bar at 60°C in the presence of a hydrogen acceptor (*e.g.*: norbornene) [214].

See also [427,538].

3.10. Hydrogen transfer reactions (organic compounds as reductants)

3.10.1. Transfer hydrogenation of C=C and C≡C bonds

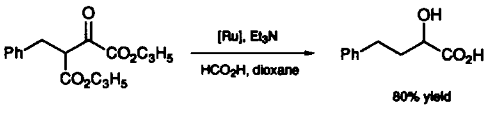
Simple alcohols, such as isopropanol and ethanol, were used for hydrogen sources in the asymmetric transfer hydrogenation of methylenesuccinic acid, 2-acetoaminocinnamic acid and some substituted acrylic acids catalyzed by $[RuH(S\text{-}BINAP)_2]PF_6$ and $RuH_2(S\text{-}BINAP)_2$. Good to excellent asymmetric induction was achieved [215]. The catalysis of hydrogen transfer in the disproportionation of 1,3-cyclohexadiene using rhodium(III) chloride catalyst precursor and deuterated 1,3-cyclohexadienes were studied [216].

See also [279].

3.10.2. Transfer hydrogenation of ketones and aldehydes

Heterobimetallic compounds $[H(CO)(PPh_3)_2Ru(\mu\text{-}BIM)M(COD)]$ (BIM = 2,2′-biimidazolate, M = Rh, Ir) were found to be more active catalysts than the mononuclear parent compounds $RuH(HBIM)(CO)(PPh_3)_2$ and M(HBIM)(COD) (M = Rh, Ir) not only for cyclohexene hydrogenation but also for the hydrogen transfer from 2-propanol to ketones and α,β-unsaturated ketones. On the basis of kinetic results it was concluded that hydrogen transfer proceeds via one metal similar to cyclohexene hydrogenation and the other metal acts as the core of a metal-ligand complex of variable electron density [217].

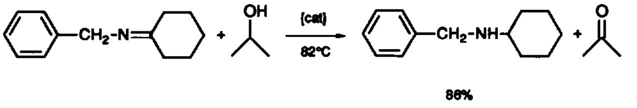
The transfer hydrogenation of glucose by various hydrogen donors at 100°C under the catalytic influence of $RuCl_2(PPh_3)_3$ gave sorbitol as major product with up to 90% selectivity [218]. The ruthenium complex-catalyzed reduction of diallyl α-oxalylcarboxylates with formic acid gave α-hydroxycarboxylic acids in good yields [219]. *E.g.*:



See also [152].

3.10.3. Transfer hydrogenation of miscellaneous organic compounds

Various imines were transfer hydrogenated by 2-propanol in refluxing solution in the presence of 5 mol% K_2CO_3 and 0.5 mol% $RuCl_2(PPh_3)_3$ [220]. *E.g.*:

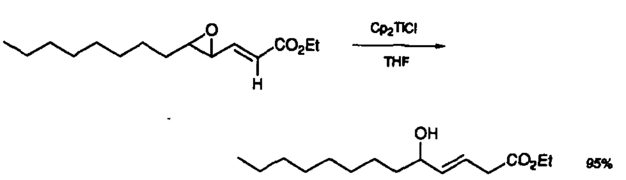


Enantioselectivities in the Meerwein–Ponndorf reduction of ketene silyl acetals using samarium alkoxides as catalysts have been examined [221].

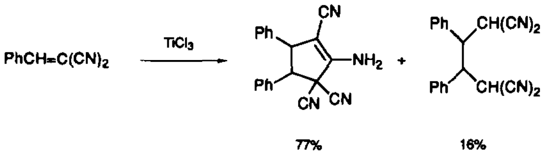
3.11. Reduction without molecular hydrogen

3.11.1. Stoichiometric reduction with low-valent transition metal complexes

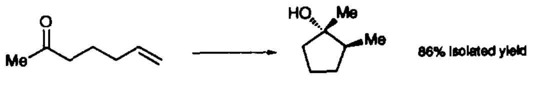
Vinyl epoxides were reduced to allyl alcohols with Cp_2TiCl at room temperature in excellent yields [222]. *E.g.*:



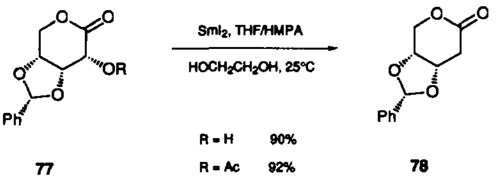
Cyclized and/or uncyclized hydrodimers were formed in the reduction of substituted dicyanoalkenes with aqueous titanium(III) chloride at 0°C [223]. *E.g.*:



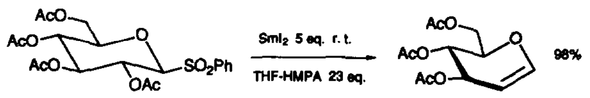
Samarium(II) iodide in the presence of HMPA effectively promotes the intramolecular coupling of unactivated olefinic ketones by a reductive ketyl–olefin radical-cyclization process [224]. *E.g.*:



A one-step deoxygenation of **77** into **78** with samarium diiodide in the presence of a proton source was reported [225].



Samarium(II) iodide in THF combined with HMPA has been used as an efficient system for the selective reduction of α,β-unsaturated esters, acids, amides, and an anhydride at room temperature [226]. Substituted pyranoid glycals were prepared by reductive elimination of glycosyl phenyl sulfones by SmI_2 + HMPA [227]. *E.g.*:



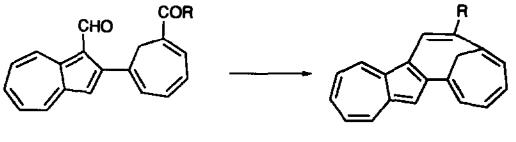
Chiral cyclopropyl halides were reduced with SmI_2 to the corresponding hydrocarbon. *E.g.*: the reaction of (*S*)-1-bromo-1-methyl-2,2-diphenylcyclopropane with SmI_2 gave 58% (*R*)-1-methyl-2,2-diphenylcyclopropane with 78% retention of the configuration [228].

The reaction of salicylaldehyde with *trans,trans*-$WH(CO)_2(NO)(PMe_3)_2$ at room temperature gave the corresponding alkoxide complex. Excess salicylaldehyde liberates the organic reduction product α,2-dihydroxytoluene [229]. The tungsten hydride *trans,trans*-$WH(CO)_2(NO)(PMe_3)_2$ was found to reduce a wide variety of β-diketones selectively to β-hydroxy ketones between 20 and 50°C [230].

See also [68,167].

3.11.2. Inorganic reductants in the presence of transition metal complexes

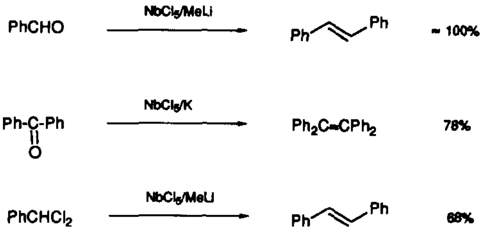
The reduction of **79** with $LiAlH_4$ in refluxing dimethoxyethane in the presence of $TiCl_3$ gave **80** [231].



79 **80**

The Cp_2TiCl_2-catalyzed reduction of *gem*-dihaloalkanes with Grignard reagent gave alkanes in the case of alkyl-substituted substrates and alkenes in the case of aryl substituents [232].

The reductive dimerization of aldehydes, ketones, benzalchloride and benzotrichloride with $NbCl_5$ + MeLi or $NbCl_5$ + K gave symmetrically substituted ethene derivatives [233].



Sodium selenite was found to enhance the catalytic activity of molybdenum(VI) oxide during the reduction of nitroarenes ($XC_6H_4NO_2$, X = 4-CN, 4-CO_2Et, H, 4-Cl, 2-Me, 3-Me, 4-Me, 4-MeO) with sodium borohydride to the corresponding amines. Under mild conditions (37°C) 86–98% yields were achieved [234].

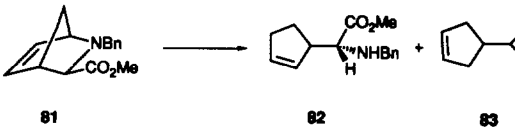
The carbon–carbon double bond of α,β-unsaturated esters such as ethyl tiglate and ethyl cinnamate was efficiently hydrogenated with $NaBH_4$ at 30°C in the presence of a catalytic amount of (TPP)MnCl, (TPP)FeCl or [T(*p*-OMe)PPFeCl (TPP = *meso*-$\alpha,\beta,\gamma,\delta$-tetraphenylporphyrinato, T(*p*-OMe)PP = *meso*-α,β,γ,4-δ-tetra(*p*-methoxy-phenyl)porphyrinato) [235]. Porphyrin-metal complexes were used to catalyze the reduction of 2-nitro-, 4-nitro- and 2,4-dinitrotoluene with dithiothreitol to the corresponding amines as a preparatory step to enhance biodegradability. 2,4,6-Trichlorophenol was oxidized by tert-butyl hydroperoxide in the presence of an iron-centered porphyrin. All organic chlorine was converted to chloride ion [236]. Highly stereoselective reductions of ethyl benzoylformate were obtained with a 1,4-dihydronicotinoyl fragment attached to the homochiral auxiliary [(η^5-C_5H_5)Fe(CO)(PPh_3)] and posessing a homochiral β-hydroxy-carboxamide at C-5 [237].

The water-soluble ruthenium phosphine complex $RuCl_2(PTA)_4$ (PTA = 1,3,5-triaza-7-phosphaadamantane) was found to be catalytically active for the reduction of unsaturated aldehydes to unsaturated alcohols in a biphasic water + chlorobenzene medium at 80°C with formate as the source of hydrogen. Under similar conditions $RhCl(PTA)_3$ is a very active catalyst for selective olefin hydrogenation using $HCO_2Na + H_2O$ or H_2 as the source of hydrogen [238].

The reduction of nitroaromatic compounds with $NaBH_4$ in the presence of soluble nickel(II) and cobalt(II) phthalocyanines as catalysts in THF + EtOH at 50°C was investigated Anilines, azocompounds and azoxycompounds were obtained in various ratios depending on the substrate and the catalyst [239].

Reduction of carbon–carbon double bonds to single bonds, and aromatic nitro compounds to amines by borohydride exchange resin was catalyzed by Ni^{2+}, Co^{2+}, Cu^{2+}, Cu^{+}, and Pd^{2+} ions in ethanol solvent. The effect of the reaction conditions were studied [240]. The kinetics of reduction of di-2-pyridyl ketone with $NaBH_4$ to di-2-pyridylmethanol have been studied in the presence of Ni^{II} and Cu^{II} [241]. Aldehydes were converted to the corresponding alcohols at room temperature with a $NiCl_2 \cdot 6H_2O + Zn/DMF + H_2O$ system [242].

In the presence of 10 mol% $Pd(PPh_3)_4$ the allylic amine **81** was reduced by $NaBH_3CN$ in refluxing THF to afford **82** and **83** in 7:1 ratio and 77% yield [243].

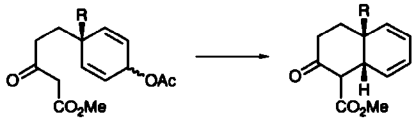


81 **82** **83**

The reduction of **84** with $NaBH_4$ in the presence of catalytic amount of $Pd(PPh_3)_4$ gave **85** in 80% yield [244].

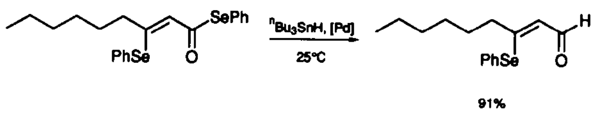
84 **85**

Treatment of **86** with 10 mol% $Pd(PPh_3)_4$ and 1.2 equiv. NaH in MeCN at 25°C gave the *cis*-decalin derivative **87** stereoselectively in 96% yield [245].



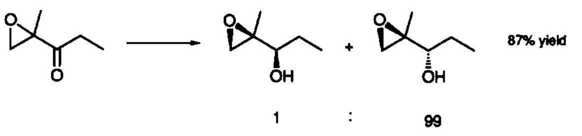
86 **87**

Palladium complexes such as $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, and $Pd(OAc)_2$ catalyze the reduction of (*Z*)-1,3-bis(arylseleno)-2-alken-1-ones with tri-n-butyltin hydride. The terminal arylseleno group is selectively reduced to afford the corresponding aldehydes in good yields [246]. *E.g.*:



The reductive dechlorination of aryl chlorides to the corresponding arenes at 25°C using $Pd(dippp)_2$ as the catalyst was investigated. High yields were obtained and various functional groups were tolerated using a reducing system containing sodium formate in alcohol or DMF [247].

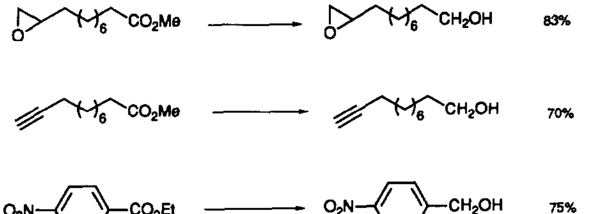
High stereoselectivity was observed in the reduction of epoxy ketones with $NaBH_4 + CeCl_3$ in MeOH at 0°C [248]. *E.g.*:



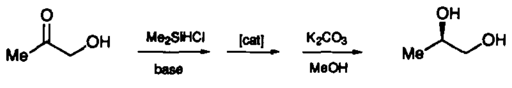
Stereocontrolled reduction of the acyl carbonyl of 2-acyl-1,3-oxathiane derivatives has been achieved by $Zn(BH_4)_2$ and $YCl_3 + NaBH_4$ [249].

3.11.3. Reduction via hydrosilylation

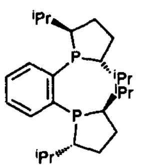
An air-stable catalyst system for the conversion of esters to alcohols was reported. Thus a combination of 5 mol% of $Ti(O^iPr)_4$ with 2.5–3.0 equiv. of $(EtO)_3SiH$ cleanly hydrosilylates esters to silyl ethers at 40–55°C, which can be converted to the corresponding primary alcohols via hydrolysis in excellent overall yield [250]. *E.g.*:



Chiral 1,2-diols were prepared from the corresponding hydroxyketones in 75–90% isolated yield and up to 93% ee through asymmetric intramolecular hydrosilylation catalyzed by a cationic rhodium(I) catalyst bearing the new chiral diphosphine (R,R)-^{i}Pr-DuPHOS (**88**) [251]. *E.g.*:



Reduction of prochiral alkyl aryl and alkyl heteroaryl ketones with diphenylsilane in the presence of neutral, cationic and zwitterionic rhodium(I) complexes as the metal catalyst and **89** as an added chiral ligand afforded the corresponding secondary alcohols in good chemical yield and low to moderate optical purity. The maximum asymmetric induction (37% ee) was observed when $Rh^+(COD)BPh_4^-$ was used as the metal catalyst [252].



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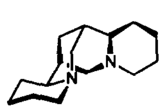
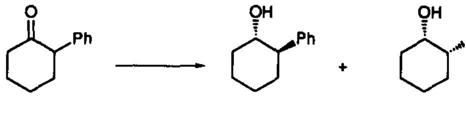


89

Stereoselectivity in reduction of substituted cyclohexanone derivatives was examined with chiral rhodium-bis(oxazolinyl)pyridine catalyst and diphenylsilane. 4-tert-Butyl-cyclohexanone gave the corresponding *trans*-(*equatorial*)-alcohol predominantly (*trans/cis* = 67/33). From **90** 99% ee of **91** and 96% ee of **92** was formed in 92% yield (*trans/cis* = 51:49) [253].



90 **91** **92**

3.11.4. Electroreduction and photoreduction

Electrochemical carbon dioxide fixation to thioester catalyzed by $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ has been reported. Thus a controlled potential electrolysis of CO_2-saturated MeCN containing the catalyst, MeC(=O)SEt, Bu_4NBF_4, and molecular sieve 3A gave MeC(=O)COO^- with a current efficiency of 27%. The reaction is strongly inhibited by the presence of H_2O and excess EtS^- [254].

The complex *cis*-$[Os(bpy)_2(CO)H]^+$ was found to be an electrocatalyst for the reduction of CO_2 to CO and formate ion in MeCN containing 0.1 M tetra-n-butylammonium hexafluorophosphate at glassy carbon or platinum electrodes [255].

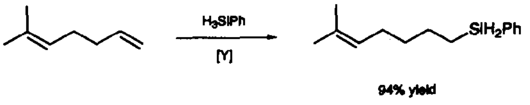
Cobalt phthalocyanine supported on a carbon gas-diffusion electrode was found to be an active and stable electrocatalyst for the selective reduction of CO_2 to CO at current densities up to 80 mA cm^{-2} [256].

Electrocatalytic reduction of the sulfur–sulfur bond in L-cystine was examined on glassy carbon electrodes coated with poly(mercaptohydroquinone) and poly(mercapto-*p*-benzoquinone) films in which Pt, Pd, Cu, Ag, and Hg thiolates were fixed. Pt and/or Pd thiolate gave the highest activity [257].

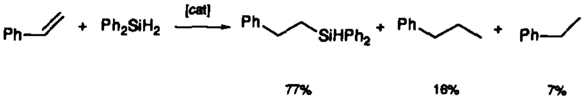
The role of configuration of adsorbed (cyclam) nickel(1 +) at mercury electrodes and its relation to the electrocatalytic reduction of carbon dioxide were investigated [258].

3.12. Hydrosilylation and related hydrometalation reactions

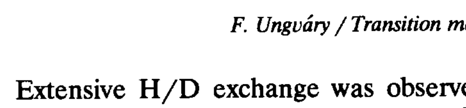
An organoyttrium complex, $(\eta^5\text{-}C_5Me_5)_2YCH(SiMe_3)_2$ was found to be an efficient and selective precatalyst for the hydrosilylation of monosubstituted and 1,1-disubstituted olefins in benzene solution at room temperature [259]. *E.g.*:



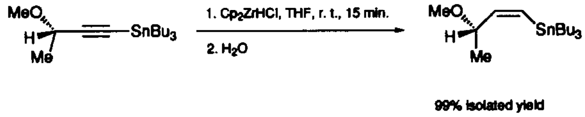
Catalysts derived from Cp_2ZrCl_2 and two equiv. of butyllithium were found to be active for hydrosilylation of olefins. In the case of styrene, three major products are formed with diphenylsilane at 25°C:



Extensive H/D exchange was observed in the hydrosilylation of styrene with Ph_2SiD_2 [260]. A new synthesis of α,β-unsaturated esters from β-ketoesters in one step was reported using Cp_2ZrHCl as stoichiometric reagent at 0°C [261]. *E.g.*:



Various stannylacetylenes were converted to *Z*-vinylstannanes via hydrozirconation [262]. *E.g.*:



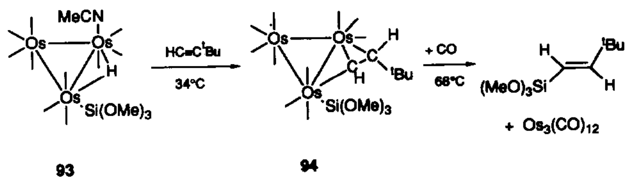
Reactions of $PhMeSiH_2$ and olefins in the presence of $Cp_2MCl_2 + {}^nBuLi$ (M = Ti, Zr, Hf) resulted products of hydrosilylation of the olefin, dehydrocoupling of the sialane to silicon oligomers, and dehydrocoupling of the silane with the olefin to form vinylsilanes. The product which dominates was found to depend on the metal and the nature of the olefin [263].

Hydrosilylation of carbonyl compounds is efficiently catalyzed by inorganic solid acids and bases such as Fe^{3+} ion-exchanged montmorillonite and hydroxyapatite at reaction temperatures between 25 and 90°C. *E.g.*: benzaldehyde and Et_3SiH gave $PhCH_2OSiEt_3$ in 94% yield [264].

The hydrido-phosphido-bridged complex $[Cp_2Fe_2(\mu\text{-H})(\mu\text{-PMen}_2)(CO)_2]$ was found to be an enantioselective catalyst in the photochemical hydrosilylation of acetophenone with Ph_2SiH_2 to give 1-phenylethanol in up to 33% ee [265].

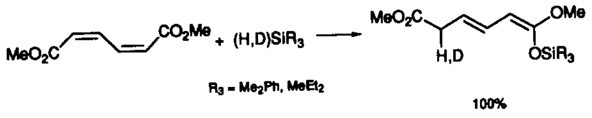
Hydrogermylation of phenylacetylene or methyl ethynyl ketone with $Ph_2HGeFeCp(CO)_2$ and $PhH_2GeFeCp(CO)_2$ in the presence of chloroplatinic acid catalyst yielded mainly the α-isomer of the adduct [266].

The isolation and structural characterization of an intermediate (**94**) in alkyne hydrosilylation by an osmium cluster complex (**93**) was reported [267].

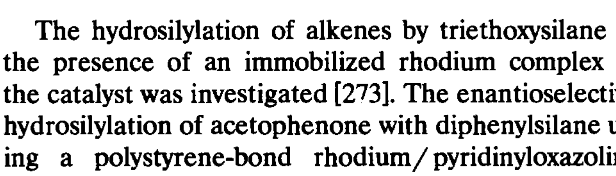


93 **94**

Vinyl-containing epoxides were selectively hydrosilylated in the presence of $RhCl(PPh_3)_3$ as the catalyst at 100–110°C, without concomitant ring opening polymerization of the epoxide groups [268]. The hydrosilylation of block styrene–butadiene rubber and nitrile–rubber using Et_3SiH in the presence of $RhCl(PPh_3)_3$ as the catalyst was investigated at 110°C in toluene. The hydrosilylation products were characterized by IR and ^{13}NMR spectroscopy [269]. Catalytic hydrosilylation of a series of organoiron acetyl complexes using dihydrosilanes in the presence of $RhCl(PPh_3)_3$ or manganese acyl complexes were reported [270]. A functionalized ketene silyl acetal was formed in hydrosilylation of dimethyl *cis,cis*-muconate in the presence of RhCl $(PPh_3)_3$ as the catalyst:



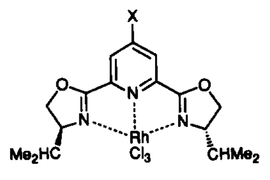
Hydrosilylation of *trans,trans*-muconate gave a 3,4-adduct [271]. Commercially available rhodium(I) compounds such as $RhCl(PPh_3)_3$, $RhCl(CO)PPh_3)_2$, $[RhCl(COD)]_2$, $[RhCl(NBD)]_2$, and $[RhCl(C_2H_4)]_2$, were used as catalyst precursors in hydrosilylation of 4-vinylcyclohexene oxide with 1,1,3,3-tetramethyldisiloxane. The product **95** was obtained in quantitative yields. There was no evidence of any competing ring-opening polymerization of the epoxy-ring [272].



95

The hydrosilylation of alkenes by triethoxysilane in the presence of an immobilized rhodium complex as the catalyst was investigated [273]. The enantioselective hydrosilylation of acetophenone with diphenylsilane using a polystyrene-bond rhodium/pyridinyloxazoline catalyst was investigated. Comparable homogeneous catalyst gave lower optical inductions [274]. Halogenated solvents such as CCl_4, PhBr, and ^{i}PrBr increased the chemical yields of products to quantitative with 33–36% ee in the $[Rh(COD)Cl]_2$ + optically active 2-pyridineoxazoline-catalyzed enantioselective hydrosilylation of acetophenone [275].

The effect of substituents at the 4-position of the pyridine skeleton in **96** on the rates and enantioselectivities of the rhodium-catalyzed hydrosilylation of ketones was studied [276].



96

Poly-γ-[*N,N*-bis(β-ethylmercaptoethyl)amino]propylsilsesquioxanerhodium immobilized on silica was found to catalyze the hydrosilylation of olefins with $(EtO)_3SiH$. The effect of reaction temperature, catalyst amount, and structure of the catalyst on activity and reusability was studied [277].

The mechanism of hydrosilation of ethene with Et_3SiH catalyzed by $CpRh(C_2H_4)(SiEt_3)H$ was studied by NMR and GC/MS methods. A mechanism involving $CpRh(SiEt_3)(CH_2CH_2SiEt_3)H$ as an intermediate was proposed [278].

Rhodium(II) perfluorobutyrate was found to catalyze the hydrosilylation of 1-alkenes under mild conditions. The mode of addition determines the products that are formed. Addition of **97** to a twofold molar excess of triethylsilane at room temperature in CH_2Cl_2 produced **98** in 52% isolated yield with 96% selectivity. When triethylsilane was added to a twofold molar excess of **97** under the same conditions **99** was obtained in 49% isolated yield with 91% selectivity.

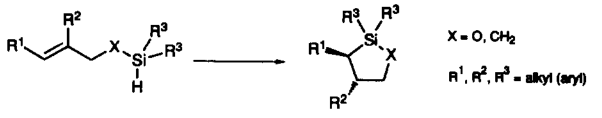
$$\underset{\mathbf{97}}{PhCH_2CH{=}CH_2} + Et_3SiH \xrightarrow{[Rh(II)]} \underset{\mathbf{98}}{PhCH_2CH_2CH_2SiEt_3} +$$

$$\underset{\mathbf{99}}{PhCH{=}CHCH_2SiEt_2} + \underset{\mathbf{100}}{PhCH_2CH{=}CHSiEt_3} + H_2$$

Compound **100** was always a minor byproduct. Catalytic hydrogenation of 1-alkenes occurred as main reaction in the presence of ethanol [279]. *E.g.*:

$$PhCH{=}CH_2 + Et_3SiH + EtOH \xrightarrow{[Rh(II)]} PhCH_2CH_3 + Et_3SiOEt$$

Enantioselective $[Rh(diphosphine)(acetone)_2]^+$-catalyzed intramolecular hydrosilylation of **101** was reported using (*S*)-BINAP (**102**) or (*S,S*)-CHIRAPHOS (**103**) diphosphine [280].



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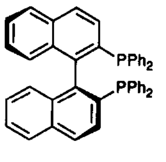

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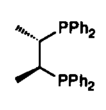
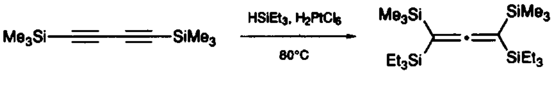


103

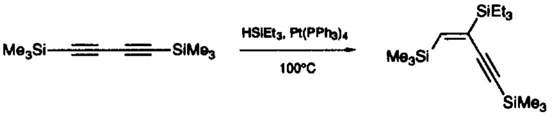
The mechanism of the reaction was investigated by the use of specifically labeled deuterated substrates [281].

Alkynes were hydrosilylated regio- and stereoselectively in the presence of *trans*-chloro(carbonyl)bis(triphenylphosphine)iridium(I) as the catalyst. For example, phenyl-acetylene and triethylsilane gave at 130°C mostly *trans*-$PhCH{=}CHSiEt_3$ with small amount of $PhC(SiEt_3){=}CH_2$ and a smaller amount of *cis*-$PhCH{=}CHSiEt_3$ [282].

Hydrosilylation of 1,4-bis(trimethylsilyl)butadiyne using various hydrosilanes and Pt^{IV}, Pt^0, Rh^I or Pd catalyst gave tetrasilylsubstituted 1,3- or 1,2-butadienes depending on catalyst and hydrosilane [283]. *E.g.*:



100%



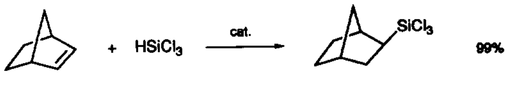
100%

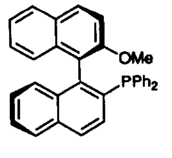
Platinum and rhodium complexes of poly(4,7-dithia-7-phenylheptylsilsesquioxane) were found to be good catalysts for hydrosilylation of alkenes with triethoxysilane [284]. The catalytic behavior of Rh^I, Pt^{II}, and Pd^{II} complexes immobilized on macroporous copolymers of acrylonitrile and divinylbenzene and terpolymers of styrene was studied in the hydrosilylation of 1-hexene. The activity of the polymer-bound catalysts strongly depend on the structure of the support used [285].

Decene, dodecene, allylbenzene, allyl phenyl ether, and allyl glycidyl ether were hydrosilylated by triethoxysilane at temperatures between 70 and 100°C in the presence of 1,1′-bis(ethylthio)ferrocene platinum and rhodium complexes as the catalysts [286,287].

Asymmetric hydrosilylation of bicycloalkenes with trichlorosilane was effectively catalyzed by 0.05 mol%

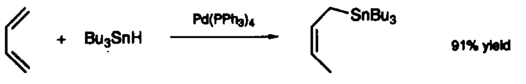
$[PdCl(\pi\text{-}C_3H_5)]_2$ and 0.02 mol% (*R*)-(+)-MOP (**104**) [288]. *E.g.*:



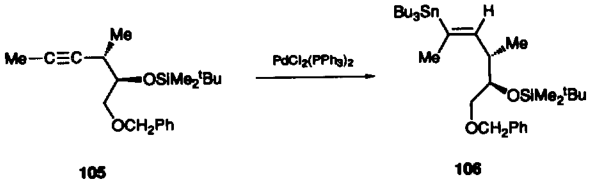


104

The mechanism of palladium(0)-catalyzed hydrostannation of conjugated dienes was studied by deuterostannation [289]. The regio- and stereoselective formation of (*Z*)-2-alkenyltributylstannanes from conjugated dienes and tributyltin hydride was catalyzed by $Pd(PPh_3)_4$ [290]. *E.g.*:



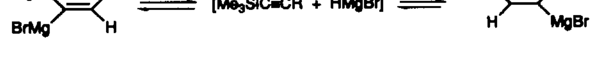
Addition of tributyltin hydride to disubstituted acetylene **105** in the presence of $PdCl_2(PPh_3)_2$ catalyst gave the *cis* addition product **106** in 70% yield [291].



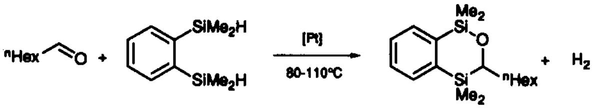
105 **106**

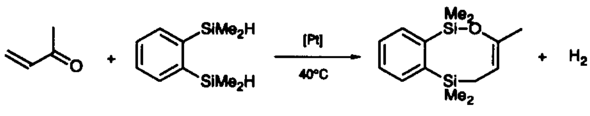
Pd^{II}, Pd^{I}, and Pd^{0} complexes were found to catalyze the addition of trichlorosilane to the olefinic bond of 1-hexene, styrene, and vinyltrichlorosilane at 80–120°C in sealed glass ampoules [292].

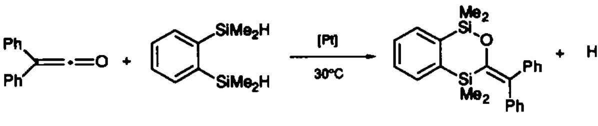
The reversibility of titanocene-catalyzed hydromagnesation of silylacetylenes has been studied [293].



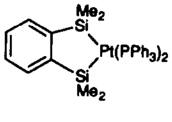
Aldehydes, ketones, and diphenylketene underwent dehydrogenative 1,2 double silylation with **107** in the presence of a catalytic amount of (ethylene)bis(triphenylphosphine)platinum or bis(dibenzylideneacetone)platinum to afford 5,6-benzo-1,4-disila-2-oxa-derivatives *E.g.*:





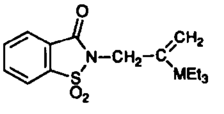


A benzodisilaplatinum(II) complex:



was suggested to be the key intermediate in those reactions [294].

The H_2PtCl_6-catalyzed hydrosilylation of norbornene with Me_2ClSiH, $MeCl_2SiH$ and $HSiCl_3$ gave the corresponding methylnorbornylchlorosilanes [295]. The hydrosilylation reaction of methacrylate with trichlorosilane in the presence of Speier's catalyst afforded γ-methacryloxypropyltrichlorosilane in *ca.* 80% yields [296]. Hydrosilylation and hydrogermylation of *N*-propargylsaccharin in the presence of Speyer's catalyst gave **108** in 75–80% yield [297].

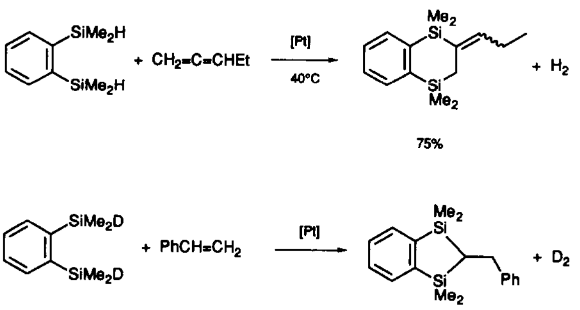


M = Si, Ge

108

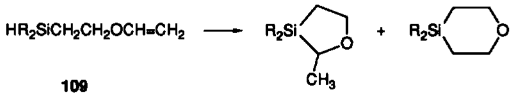
Crosslinked polyacrylate-supported sulfide platinum complexes were found to show high catalytic activity and stability in the hydrosilylation of olefins by triethoxysilane at 80–100°C [298].

The H_2PtCl_6-catalyzed addition reactions of Pr_3SiH, Pr_2SiClH, Pr_2SiFH, $PrSiCl_2H$, and $PrSiF_2H$ with vinyl or allyl acetates, or methyl or butyl methacrylates were studied. The reactions gave 30–40% yields of the *anti*-Markovnikov addition products [299]. With $Pt(CH_2{=}CH_2)(PPh_3)_2$ as catalyst precursor various olefins and dienes gave dehydrogenative double silylation with *o*-bis(dimethylsilyl)benzene [300]. *E.g.*:



The relative rates of platinum-catalyzed hydrosilylation of terminal olefins *vs.* internal alkynes were compared in competitive reactions using equimolar amounts of either $(EtO)_3SiH$ or $Me_3SiOSiMe_2H$ [301].

In the presence of chloroplatinic acid, **109** gave five- and six-membered cyclic products in moderate yields [302].



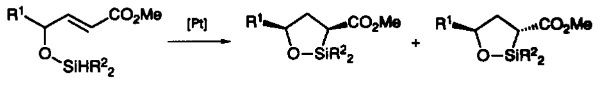
109

The catalytic hydrosilylation of acetophenone with $MeSiHCl_2$ or $MePhSiH_2$ in the presence of platinum (II) complexes with sulfoxide and mixed (olefin, amine, phosphine) sulfoxide ligands was studied [303]. The catalytic activity of a complex obtained from potassium chloroplatinite and 10-selenabenzo-15-crown-5 was investigated for the hydrosilylation of olefins by triethoxysilane [304].

Silica-bound poly-4,7-dithianonylsesquisiloxane platinum complex exhibited a high catalytic activity on the hydrosilylation of olefins with triethoxysilane. Turnover number as high as 80000 was found [305].

Hydrosilylation catalyzed by hexachloroplatinic acid was used to introduce tertiary amino groups in polybutadiene. The kinetics of the reaction were investigated. At low silane concentration the reaction is first-order in Pt, second-order in silane and zero-order in vinylic double bounds. The apparent rate constant is inversely proportional to the concentration of amino groups [306]. Mechanistic studies of platinum-catalyzed hydrosilylation of vinylmethylsiloxane compounds with various silicon hydrides were reported [307].

The effect of substituents on the diastereoselectivity of the platinum complex-catalyzed intramolecular hydrosilylation reaction of **110** was investigated. The diastereoinduction was sensitive to the bulk of the allylic substituent, but not to the groups on silicon [308].



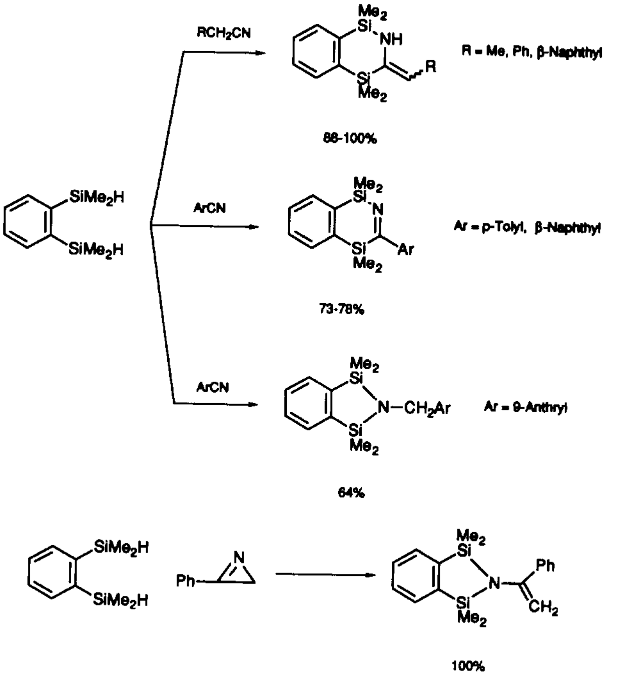
110

In the presence of platinum-containing catalysts a series of new racemic vinylsilanes **111** and **112** were obtained by hydrosilylation of acetylene and substituted alkynes with (±)-$N(CH_2CH_2O)_3SiCH_2PhMeSiH$ [309].

$$R_3SiH + HC{\equiv}CR' \xrightarrow[25\text{-}100°C]{[Pt]} \underset{\mathbf{111}}{H_2C{=}CR'(SiR_3)} + \underset{\mathbf{112}}{R_3SiCH{=}CHR'}$$

$R' = H, Ph, CO_2Me, CMe_3, SiMe_3$

Nitriles and 2-phenylazirine undergo dehydrogenative double silylation with *o*-bis(dimethylsilyl)benzene in benzene or toluene solution in the presence of $Pt(CH_2{=}CH_2)(PPh_3)_2$ catalyst to give a new class of heterocyclic compound [310].

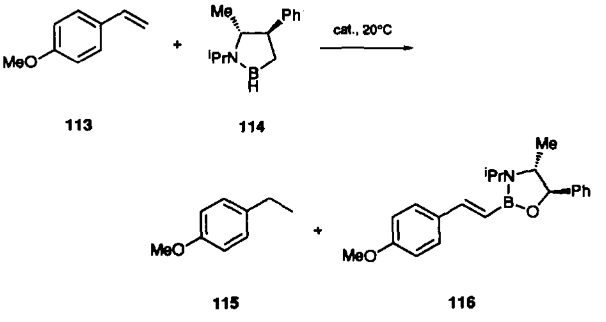


See also [112].

3.13. Hydroboration

Synthetic applications and mechanistic studies of the transition metal-catalyzed hydroboration reaction were published [311]. Organolanthanide complexes $(\eta^5\text{-}Me_5C_5)_2LnR$ (Ln = La, Sm; R = H, $CH(SiMe_3)_2$), and $(\eta^5\text{-}Me_5C_5)_2Sm(THF)$ catalyze the catecholborane hydroboration of a wide range of olefins including terminal, terminal or internal disubstituted, and trisubstituted olefins [312].

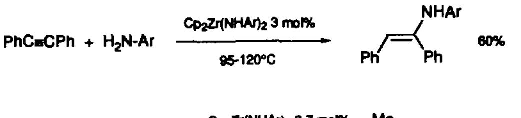
The (bis-alkene)rhodium complex-catalyzed reaction of **113** and **114** led exclusively to coproduction of **115** and **116** [313].



113 **114** **115** **116**

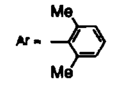
The rhodium catalyzed hydroboration reaction has been applied in the stereoselective reduction of *N*-acylimidates [314]. Multinuclear NMR spectroscopy was used to examine the primary products from catalyzed hydroborations of alkenes with catecholborane using a variety of rhodium phosphine complexes [315]. Multinuclear NMR spectroscopy was used to investigate reactions of catecholborane with $RhCl(PPh_3)_3$. Examination of product and label distributions provided mechanistic insight into catalyzed alkene hydroborations [316]. The scope and synthetic applications of the rhodium(I)- and iridium(I)-catalyzed hydroboration of olefins with catecholborane were investigated [317]. The mechanism of the $RhCl(PPh_3)_3$-catalyzed olefin hydroboration with catecholborane by deuterium labeling experiments was studied [318].

Allenylboranes were prepared in up to 92% yield by palladium(0)-catalyzed hydroboration of 1-buten-3-ynes [319]. *E.g.*:

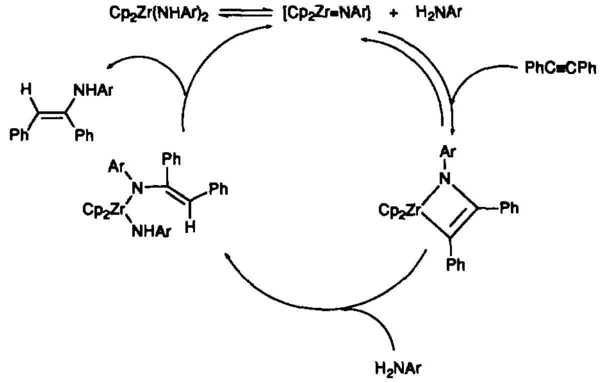


3.14. Hydroamination

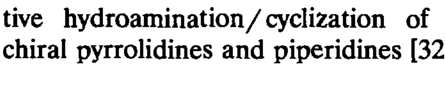
Stoichiometric and catalytic hydroamination of alkynes and allene by zirconium bisamides $Cp_2Zr(NHR)_2$ were reported. *E.g.*:



Kinetic results are consistent with a reversible rate-determining α-elimination of amine and generation of the transient imido complex $Cp_2Zr{=}NR$. A mechanism for the catalytic cycle was suggested [320].



The organolanthanide-catalyzed hydroamination has been studied in a kinetic, mechanistic, and diastereoselectivity study of the cyclization of *N*-unprotected amino olefins. *E.g.*: in the presence of $Cp'_2LaCH(SiMe_3)_2$ as the precatalyst the intramolecular cyclization of **117** afforded **118** with 95/hour turnover frequency at 25°C. It was suggested that olefin insertion into the La–N bond of the amino–amido complex is turnover-limiting and is followed by a rapid protonolysis of the resulting La–C bond. The catalyst at high amine concentrations was postulated to be a La(amido)(amine)$_2$ complex [321].

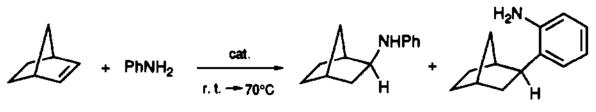


117 **118**

Chiral organolanthanide complexes $Me_2Si(Me_4C_5)(C_54\text{-}H_3R^*)LnE(SiMe_3)_2$ (R^* = (−)-menthyl, (+)-neomenthyl; Ln = La, Sm; E = N, CH) were used as precatalysts for the enantioselective or diastereoselective hydroamination/cyclization of aminoolefins to chiral pyrrolidines and piperidines [322].

R = Me, H; n = 1
R = Me; n = 2

The reaction of aniline with norbornene in the presence of a catalytic system generated from $[\{Rh(PEt_3)_2Cl\}_2]$ and PhNHLi gave **119** as minor product and **120** as major product.

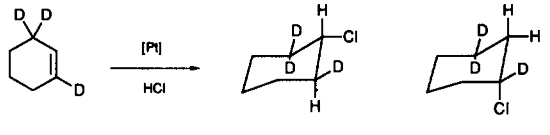


119 (15%) **120** (30%)

Using diphenylamine and Ph_2NLi the catalytic reaction gave only the corresponding hydroarylated product in moderate yield [323].

3.15. Hydrochlorination and hydroselenation

Catalytic hydrochlorination of olefins at room temperature in toluene solution in the presence of $PtCl_2(CO)(C_6H_{10})$, *cis*-$PtCl_2(CO)_2$ or $Pt_2Cl_4(CO)_2$ as catalyst precursor has been reported. Hydrochlorination of cyclohexene-1,3,3-d_3 (**121**) gave the *syn* addition products (**122**) and (**123**), no *anti* product being observed, in contrast with the results of the hydrochlorination of the same substrate in glacial acetic acid with anhydrous HCl [324].



121 **122** (48%) **123** (52%)

The hydroselenation of acetylenes was found to be catalyzed by a variety of transition metal complexes. For example, the palladium acetate-catalyzed reaction of 1-octyne with benzeneselenol gave 2-phenylseleno-1-octene as the major (62%) product [325].

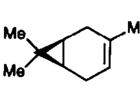
4. Oxidation

4.1. Catalytic oxidation of hydrocarbons and hydrocarbon groups with O_2

4.1.1. Oxidation of saturated hydrocarbons The air-oxidations of light alkanes catalyzed by first-row transition-metal phthalocyanine and porphyrin complexes were studied [326]. The results of the oxidation of propene and cyclohexane by dioxygen in ethyl acetate or benzene in the presence of propionaldehyde and first-row transition-metal *p*-tetratolylporphyrins as catalysts were summarized [327]. The oxygenation of cyclohexane, ethylbenzene, and styrene with dioxygen catalyzed by porphyrin metal complexes in the presence of ferrocene as reducing agent was investigated [328].

Manganese–porphyrinate immobilized on a perfluorinated sulfonated copolymer with a morpholine bridge was found to be a more active and stable catalyst in cholesterol oxidation than the monomeric metalloporphyrin [329].

The Gif oxidation ($FeCl_2 \cdot 4H_2O + Zn +$ air) of **124** in pyridine + AcOH gave a mixture of **125**, **126** and **127** [330].



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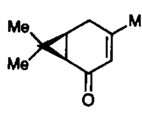

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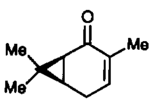

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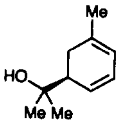


127

The mechanism of alkane functionalization at nonheme iron centers was studied [331]. Linear and branched alkanes were catalytically monooxygenated to a mixture of alcohols and carbonyl compounds at 25°C under 1 bar dioxygen using iron(III) chloride + pyrochatechol + hydroquinones + pyridine system in acetonitrile [332].

The oxidation of alkanes such as methane by dioxygen in the presence of a binuclear μ-hydroxo iron complex immobilized on imidazole modified silica as the catalyst was studied [333]. The oxidation of alkanes by dioxygen was investigated in the presence of silica-supported binuclear iron complex as a catalyst, zinc as a reducing agent, methylviologen as a mediator, and acetic acid as an effector [334].

(μ-Oxo-μ-carboxylato)diiron(III) complexes with bipyridine ligands such as $[Fe_2O(bpy)_2(OAc)_2(H_2O)_2](ClO_4)_2 \cdot 1.8NaClO_4$ were found to be active catalysts for the oxidation of methane, ethane, and cyclohexane. Deuterium isotope effect and cyclohexane/cyclopentane relative rate studies indicate that a mononuclear perferryl iron complex is the active species [335]. Various iron complexes having μ-oxo bridges were examined for catalytic activity in alkane hydroxylation with air or oxygen in both liquid and vapor phase. The conversion of μ-oxo to ferryl oxo species may be the key to catalytic activity in some instances [336].

Various alkanes and alkylated arenes were catalytically oxidized with molecular oxygen (1 bar) at room temperature to a mixture of the corresponding alcohol and ketone using iron powder, $Fe(OAc)_3$, $FeCl_3 \cdot 6H_2O$, $RuCl_3 \cdot nH_2O$ or $RuCl_2(PPh_3)_3$ as the catalyst precursor and acetic acid as the co-catalyst in the presence of heptanal or an other aldehyde [337].

The kinetics of oxidation of cyclohexane to cyclohenanol and cyclohexanone, and adamantane to 1-adamantanol, 2-adamantanol and 2-adamantanone with molecular oxygen catalyzed by $Ru^{II}(saloph)Cl_2^-$ complex were reported [338]. The kinetics of oxygenation of cyclohexene, cyclooctene, and styrene to the epoxide and of cyclohexane and toluene to alcohols in the presence of $[RuCl_2(H_2O)_4]^+$ as the catalyst were investigated [339].

The oxidation of adamantane by dioxygen catalyzed by Ru^{III}-EDTA in a 1:3 (v/v) mixture of water and 1,4-dioxane was investigated. The oxidation reactions leading to 1-adamantanol, 2-adamantanol and 2-adamantanone were shown to proceed through dioxygenase and monooxygenase routes in the absence and presence of ascorbic acid, respectively [340]. Oxidation of ethyl-, propyl-, and butylbenzene by air or dioxygen at 100°C and 1 bar catalyzed by polymer-supported ruthenium 2,2′-bipyridine complexes gave the corresponding ketone, PhCOR, as the major product. The ketone selectivity increased to 89.4% with an increase in side chain length [341]. Methane, ethane and propane was oxidized by cobalt(III) trifluoroacetate at 130–180°C and 10–40 bar to give the corresponding trifluoroacetic acid ester, respectively, in 80–90% selectivity. The reactions are catalytic in the presence of dioxygen [342]. The induction period in the oxidation of 2,4-dichlorotoluene by dioxygen in the presence of cobalt stearate was reduced by the addition of peroxides, 2,4-dichlorobenzoic acid, tetrabromoethylene, or benzaldehyde [343]. The liquid-phase catalytic oxidation of 1,2-diphenylethane with oxygen in acetic acid at 110°C containing a Co + Mn + Br catalyst gave benzil with > 80% selectivity [344].

A combination of platinum(II) ion and metallic platinum was found to oxidize ethane to a mixture of acetic and glycolic acids in aqueous medium in the presence of dioxygen. The platinum(II) ion was found to be responsible for the initial C–H activation step leading eventually to the formation of ethanol and ethylene glycol, while metallic platinum catalyzes the subsequent air oxidation of the alcohols to the corresponding acids [345].

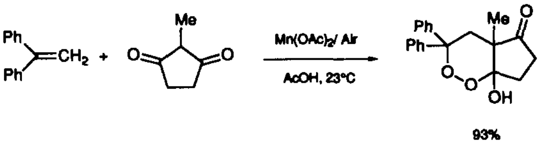
Saturated cyclic hydrocarbons were transformed into the corresponding homologous carboxylic acid by $Cu^0 + CO + O_2$ or $Fe^0 + CO + O_2$ in pyridine/acetic acid at room temperature and 2 bar total pressure [346]. Oxidation of cyclohexene with dioxygen (1 bar) in the presence of copper-polymer-bound 2,2′-bipyridine complexes at 60°C gave 2-cyclohexen-1-ol and 2-cyclohexen-1-one with 15–40% conversion and 85.2–95.7% total selectivity [347].

See also [365,371,373].

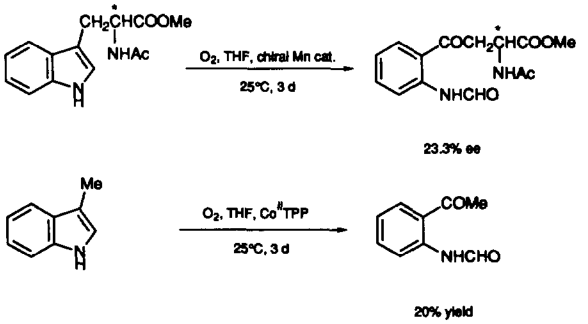
4.1.2. Oxidation of olefins

The oxidation of cyclohexene with dioxygen in the presence of $VO(DMSO)_4(SCN)$ as the catalyst was studied. The rate of cyclohexene oxidation was found to be independent of the catalyst concentration [348].

The reaction of 1,1-diphenylethene, 1,3-dicarbonyl compounds and molecular oxygen in the presence of manganese(II) acetate yielded the corresponding cyclic peroxides in moderate-to-good yields [349]. *E.g.*:

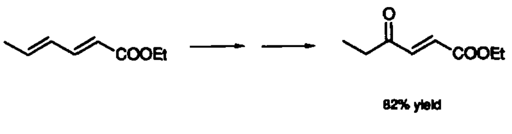


The catalytic and stereoselective activities of manganese, iron, and cobalt achiral and chiral porphyrines in dioxygenation of tryptophan derivatives and tryptophan analogues have been investigated [350]. *E.g.*:



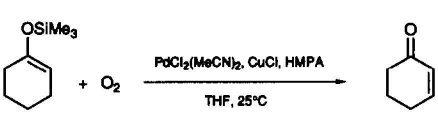
The oxidation of 1-hexene to 2-hexanone and cyclohexene to cyclohexene oxide by molecular oxygen were catalyzed by $[Ru^{III}(EDTA)(NO)]$ in an ethanol + water medium in the temperature range 30–45°C [351,352].

Direct oxidation of aryl-substituted olefins to ketones at room temperature with O_2 and Et_3SiH in 2-PrOH + CH_2Cl_2 solution in the presence of cobalt(II) porphyrin as a catalyst was reported [353]. Ester, amide, and nitrile derivatives of 2,4-alkadienoic acids were converted to the corresponding 4-oxo-2-alkenoic acid derivatives in good yields by the oxygenation with dioxygen and triethylsilane at 28°C in the presence of a catalytic amount of [5,10,15,20-tetra(2,6-dichlorophenyl)porphinato]cobalt(II) followed by acetylation [354]. *E.g.*:



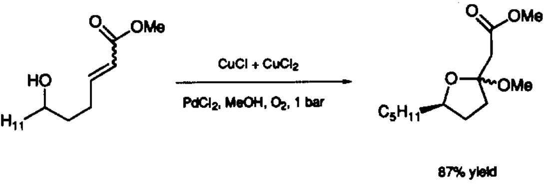
Liquid-phase oxidation of α-pinene by dioxygen catalyzed by cobalt stearate afforded *trans*-verbenol and verbenone. The effect of temperature and substrate and catalyst concentration on the reaction was studied and a rate equation deduced [355]. Mechanistic studies on the oxygenation of cyclooctene at $[\{RhCl(C_8H_{14})_2\}_2]$ in benzene containing *cis*-$[5\text{-}^2H_1]$-cyclooctene have shown by ^{13}C NMR analysis, that the monodeuterioisotopomers of cyclooctanone have been formed by oxygenative attack on the vinylic carbon rather than on the allylic centers or on π-allylic intermediates [356].

Terminal alkenes such as 1-decene were oxygenated to methyl ketones under atmospheric pressure of O_2 using $PdCl_2(MeCN)_2$, CuCl and HMPA catalyst system at 50°C in 1,2-dichloroethane. Using this catalyst system, cyclopentene was similarly converted into cyclopentanone (47%), and styrene gave acetophenone (80%) together with benzaldehyde (18%). However, no O-atom transfer occurred with silyl enol ethers, such as **128**. Instead, the silyl group was oxidatively eliminated to give **129** [357].

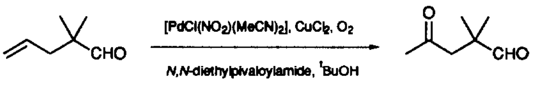


128 **129**

The Wacker oxidation of α,β-unsaturated esters was employed in the one step preparation of masked β-ketoester under almost neutral reaction conditions [358]. *E.g.*:

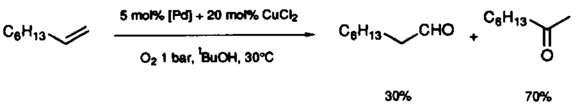


The Wacker type oxidation of α-olefins with $PdCl(NO_2)(MeCN)_2$, $CuCl_2$ and O_2 was improved by using bulky amides as (co-)solvents. *E.g.*: a quantitative oxidation of **130** to **131** was achieved using 0.4 mol% *in situ* prepared catalyst and 8 hour reaction time at 30°C and 1 bar [359].



130 **131**

Solutions of $[Me_2C(OH)CH_2CONMe_2]Pd(Cl)NO_2$ were found to catalyze the oxidation of alkenes with dioxygen [360]. *E.g.*:



See also [210,328,371,412].

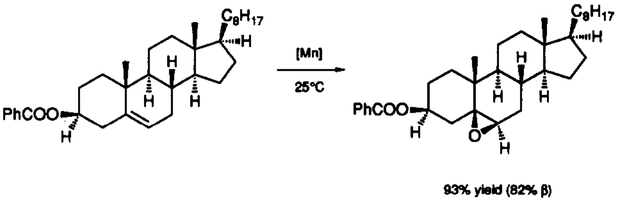
4.1.3. Epoxidation of olefins

The epoxidation of cyclohexene, 1-octene, *cis*-4-octene, 3-ethyl-1-pentene, and 2,4,4-trimethyl-1-pentene was investigated in the presence of $MoO_2(acac)_2$, MoO_3 and other oxides as catalysts [361].

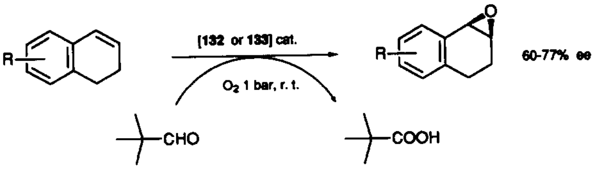
The kinetics of epoxidation of refined soybean oil by O_2 using molybdenum acetylacetonate catalyst were studied as a function of temperature, catalyst concentration and degree of unsaturation [362]. The catalytic activity of $[W_3O_2(AcO)_6(H_2O)]Br \cdot 2H_2O$ and $[W_2MoO_2(AcO)_6(H_2O)]Br \cdot 2H_2O$ in the oxidation of styrene with dioxygen have been studied. The results showed that these two clusters have better catalytic properties than those given by $IrCl(CO)(PPh_3)_2$ and $RhCl(PPh_3)_3$ [363].

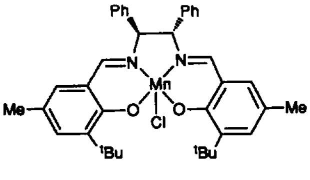
The oxygenation of *trans*-2-phenyl-1-vinylcyclopropane using Mn^{III}-salen complexes as catalysts gave high yields of the corresponding epoxide. A concerted reaction mechanism was suggested [364]. Selective oxygenations of hydrocarbons and thioethers by dioxygen with Mn(TPP)Cl + 1-methylimidazole system using zinc as electron donor and carboxylic acids as proton donor were studied. Epoxidation of olefins (34–58% yield), hydroxylations of alkenes (1–36% yield), and oxidation of thioethers to the corresponding sulfoxides (up to 68% yield) were reported [365].

In the presence of a catalytic amount of bis(dipivaloylmethanato)manganese(II), various cholesterol derivatives were converted into the corresponding β-epoxide in good to high yields with combined use of molecular oxygen and isobutyraldehyde [366]. *E.g.*:

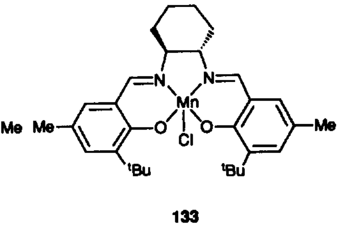


Optically active Mn^{III}-salen complexes (**132, 133**) were used as catalyst in the enantioselective epoxidation of unfunctionalized olefins with combined use of molecular oxygen as oxidant and pivalaldehyde as co-reductant [367].





132



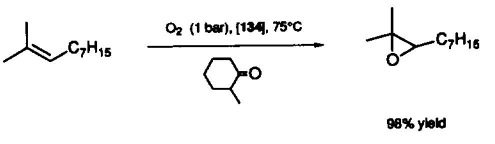
133

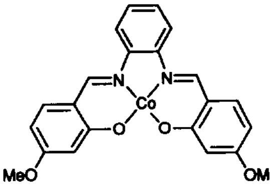
Cyclohexene oxide was obtained by the addition of benzylviologen bromide in the air-equilibrated acetonitrile solution containing $Mn^{III}(TPP)Cl$, zinc powder, benzoic anhydride and cyclohexene [368]. 2,6-Permethylated β-cyclodextrin-linked iron and manganese porphyrins were found to catalyze the enantioselective oxygenation of a racemic mixture of (S)-α-pinene and (R)-α-pinene with molecular oxygen at 25°C under irradiation with visible light. Up to 67% ee in epoxide and in various monooxygenated products was reported [369].

A solvent effect in the oxygenation reactions of *cis*-stilbene in the mixed solvents, acetonitrile + benzene, acetonitrile + dichloromethane, and acetonitrile + carbon tetrachloride catalyzed by $Fe(MeCN)_6 \cdot (ClO_4)_2$ and $Fe^{III}(TPP)Cl$, resulted in significant changes of the product ratio [370].

The oxidation of cyclohexane to cyclohexanol, cyclohexanol to *cis*-1,3-cyclohexane diol and cyclohexene to epoxide by Ru^{III} + EDTA + ascorbate + O_2 system was studied. The order of the reactivity was cyclohexene > cyclohexanol > cyclohexane [371]. The Ru^{III} + EDTA + ascorbate + O_2 system was found to catalyze the epoxidation of olefins in water/dioxane (1/2, v/v) at 30°C in the presence of an acid. The reactivity of the olefins was observed to decrease in the order: *cis*-cyclooctene > styrene > *trans*-stilbene [372]. Based on kinetic results a μ-peroxoruthenium(IV)-substrate complex $[Ru^{IV}(EDTA)(S)]_2O_2^{2-}$ was suggested as intermediate in oxygenation reactions of saturated and unsaturated substrates by molecular oxygen catalyzed by $K[Ru(EDTA\text{-}H)Cl] \cdot 2H_2O$ [373]. The kinetics of the $[Ru^{III}(EDTA)(H_2O)]^-$-catalyzed epoxidation of styrene and substituted styrenes with molecular oxygen in 50% water + dioxane medium were studied. The rate of epoxidation was found to be first order with respect to the catalyst complex and substrate concentrations and one-half order with respect to dissolved oxygen concentration. At high substrate concentrations a zero-order dependence of rate with respect to substrate concentration was found in each case [374].

The epoxidation of cyclohexene in cooxidation with propionaldehyde were studied using heterogenized-homogeneous metal-ion resin catalyst. The cobalt-type resin was found to be the most active catalyst giving 89% selectivity to cyclohexene oxide at 92% conversion [375]. Di- and trisubstituted olefins were oxygenated into the corresponding epoxides in good to high yields by combined use of molecular oxygen (1 bar) as the oxidant, cyclic ketones as the reductant and cobalt(II)-Schiff base complexes as the catalyst [376]. *E.g.*:





134

Alkenes were oxidized to epoxides stereospecifically, alcohols were oxidized to aldehydes for terminal alcohols, and to ketones for internal alcohols, tetrahydrothiophene and tetrahydrothiophene S-oxide were oxidized to sulfoxide and sulfone, respectively with molecular oxygen (1 bar) at 25°C in DMF in the presence of triphenyl phophine and $[Co_2(\mu\text{-}OH)L]$ (H_3L = 2,6-bis[(2-hydroxyphenyl)iminomethyl]-4-methylphenol) as the catalyst. Triphenyl phosphine was cooxidized. Under the same conditions diphenyl acetylene was converted to benzil [377].

The β-diastereofacial selectivity in air-epoxidation of cholesterol and cholesteryl acetate was found to be more than 80% in the presence of $(TPP)Ni^{II}$ [378].

See also [339,351,352,704].

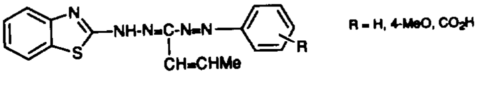
4.1.4. Oxidation of aromatics

Cerium(III) acetate was found to catalyze the selective liquid-phase oxidation of 2,5-dimethoxy-*p*-cresol at 120°C and 3 bar dioxygen in methanol to 4-hydroxy-3,5-dimethoxybenzaldehyde. Yields higher than 95% were reported [379].

The oxidation of cumene using hemin as the catalyst immobilized on the surface of various nitrogen-containing organosilicas was studied [380].

A kinetic study of the oxidation of 2,4-dichlorotoluene in the presence of a $Co^{2+} + Mn^{2+} + Br^-$ catalyst in the initiation and propagation steps [381]. S-alkylthiuronium salts were applied as phase-transfer catalysts in the $CoBr_2$-catalyzed oxidation of *p*-xylene by dioxygen [382].

Kinetics and mechanism of cumene oxidation by dioxygen in aqueous solutions of sodium dodecyl sulfate were studied in the presence of copper sulfate [383]. Copper complexes with ligand **135** have a high catalytic activity toward the oxidation of anthracene to the peroxide [384].

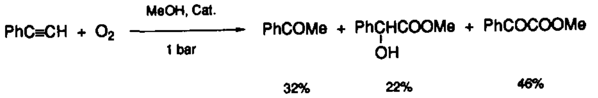


135

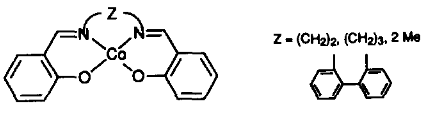
4.1.5. Oxidation of Alkynes

The oxygenation of various alkynes in alcohols at 60°C was studied by using cobalt-Schiff base complexes

(**136**) as catalysts. Incorporation of monooxygen and the alcohol into the triple bond without any carbon–carbon bond cleavage was observed [385]. *E.g.*:



$$PhC{\equiv}CH + O_2 \xrightarrow[\text{1 bar}]{\text{MeOH, Cat.}} \underset{32\%}{PhCOMe} + \underset{22\%}{Ph\underset{OH}{C}HCOOMe} + \underset{46\%}{PhCOCOOMe}$$



136

See also [377].

4.2. Catalytic oxidation of O-containing organic compounds with O_2

4.2.1. Oxidation of alcohols

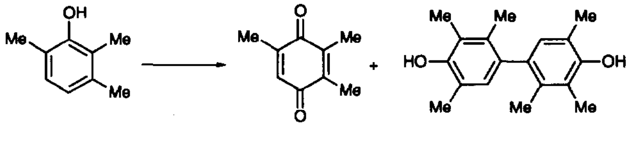
The effect of acidity and basicity on the catalytic activities of six 12-tungstophosphoric acids with Keggin structure in the oxidation of benzyl alcohol was studied. Optimal reaction conditions were elaborated [386].

The kinetics of the copper complex-catalyzed aerobic oxidation of ascorbic acid were investigated [387]. The kinetics of the copper-catalyzed oxidation of ascorbic acid in aqueous acetonitrile were studied. At sufficiently high acetonitrile concentration, the rate of the overall reaction is given by the rate of Cu^{I} autoxidation. It is first order with respect to $[Cu^{I,\,II}\ \text{tot}]$ and $[O_2]$ and shows an inverse-square dependence on [MeCN] [388]. Copper(II) complexes such as $Cu(acac)_2$ and $[Cu(bpy)(H_2O)_2](ClO_4)_2$ were found to be effective catalysts for the oxidation of aromatic and aliphatic alcohols to aldehydes and ketones [389]. The catalytic oxidation of cyclohexanol with dioxygen in the presence of various Cu^{II} complexes and different basic co-catalysts were studied [390]. The catalytic oxidation of benzyl alcohol by a system containing Cu^{II}-(picolinate)$_2$ + O_2 + NaOH was studied. Addition of Fe^{2+} accelerated the oxidation [391].

See also [377,545].

4.2.2. Oxidation of phenols

In the presence of heteropoly acids $H_{3+n}PMo_{12-n}V_nO_{40}$ the oxidation of **137** by dioxygen in AcOH + H_2O gave up to 86% **138** and some **139**. **139** was shown to be an intermediate in the oxidation of **137** to **138**, and its yield increases at the expense of **138** with increasing H_2O content of the solvent [392].



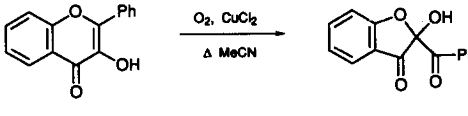
137 **138** **139**

The heteropolyanion $[PV_2Mo_{10}O_{40}]^{5-}$ was found to catalyze the selective aerobic oxidation of dialkylphenols to diphenoquinones and the oxidation of 2,3,5-trimethylphenol to the 2,3,5-trimethyl-1,4-benzoquinone at 25–60°C in n-hexanol or in other alcohols. The oxidation potential of the substrate correlates with the rate [393].

Oxidation of 2,6-di-tert-butylphenol by dioxygen catalyzed by superoxo type pentadentate Schiff base cobalt(III) complexes gave 2,6-di-tert-butylbenzoquinone as a major product. The activated oxidation catalysts were generated by the treatment of pentadentate Schiff base cobalt(II) complexes with the oxygen-saturated DMF solution [394]. The efficiency of new cobalt porphyrin polymers as catalysts was compared to already described systems in oxidation of 2,6-di-tert-butylphenol by molecular oxygen [395].

The catecholate complex $[(triphos)Ir(DTBC)]^+$ (triphos = $MeC(CH_2PPh_2)_3$; DTBC = 3,5-di-tert-butylcatecholate) was found to be an effective homogeneous catalyst for the selective oxidation of $DTBCH_2$ to 3,5-di-tert-butyl-*o*-quinone by molecular oxygen. The reaction is first order with respect to catalyst and substrate concentrations and zero order with respect to the partial pressure of dioxygen in the range of 1–50 bar. Kinetic and thermodynamic data are consistent with a rate-determining step involving the attack of free catechol to the dioxygen adduct $[(triphos)\overline{Ir(\overline{OO)}DTBSQ)}]^+$ (DTBSQ = 3,5-di-tert-butylsemiquinonate) [396].

Copper(II) ion encircled by a bis-branched oligomeric urea ligand effectively catalyzes oxidative coupling of various substituted phenols (2,6-di-tert-butylphenol, 2,6-di-tert-butylcresol, and 2,6-dimethylphenol) in the presence of dioxygen. The final oxidation product is the corresponding quinone [397]. The oxidation of catechol to *o*-quinone by molecular oxygen in the presence of catalytic amounts of copper(II) ions was studied by use of a Clark-type oxygen electrode and spectrophotometric methods at 25°C. The observed kinetic data were explained in terms of a chain reaction involving the copper(I)-dioxygen species CuO_2^+, which reacts with the free ligand and its copper(II) complexes [398]. The reaction of **140** with dioxygen in the presence of CuCl and $CuCl_2$ were studied. Using $CuCl_2$ in the reaction, **141** was formed in 80% yield [399].

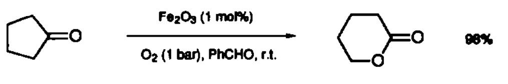


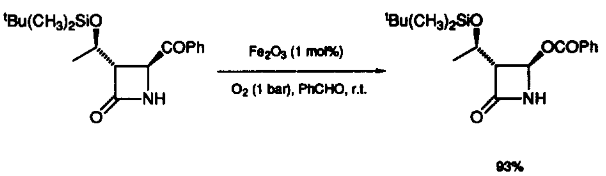
140 **141**

The stoichiometric and catalytic oxidation reactions of hydroquinones, phenols, 3,5-di-tert-butylcatechol, and 3,4-dimethylaniline with macrocyclic binuclear copper complexes were studied [400]. 2,4,6-Trimethylphenol and 2,6-dimethylphenol were effectively oxidized to trimethyl-*p*-benzoquinone and 2,6-dimethyl-*p*-benzoquinone, respectively, with molecular oxygen in the presence of a catalytic amount of copper(II)-chloride-amines in alcohol at 60°C. Among the amines hydroxylamine hydrochloride and acetone oxime coupled with hydrochloric acid gave the best results (up to 93% yield) [401]. Copper(II) complexes containing the tripodal ligand tris(3,5-dimethylpyrazol-1-ylmethyl)amine were found to be catalytically active in the oxidation of catechol to quinone [402]. Copper complexes immobilized to chitosan were found to catalyze the air oxidation of catechol derivatives [403]. The kinetics of oxidation of hydroquinone in methanol/water at 25°C catalyzed by pyridine-Cu^{II} complexes attached to polyorganosiloxanes were investigated. The catalytic oxidations followed Michaelis–Menten-like kinetics [404].

4.2.3. *Oxidation of aldehydes and ketones*

The Fe_2O_3-catalyzed oxidation of ketones with molecular oxygen (1 bar) in the presence of an aldehyde at room temperature gives the corresponding lactones or esters in high yield [405]. *E.g.*:





93%

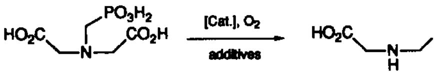
Aromatic and some aliphatic aldehydes were transformed to the corresponding carboxylic acid in the presence of catalytic amount of cobalt(II) chloride, molecular oxygen and acetic anhydride at room temperature [406]. A study of the Co^{II}-catalyzed autoxidation of benzaldehyde has shown how the various cobalt-containing species (a mixed-valency oxo-centered trimer, a cobalt(III) oxo-centered trimer, or a hydroxo-bridged cobalt(III) dimer) change as reaction takes place [407].

Oscillatory or chaotic dynamics were found for the $Co(OAc)_2$-catalyzed air oxidations of benzaldehyde, cyclohexanone, toluene, and *p*-xylene [408]. The oscillatory behavior of the autoxidation of benzaldehyde catalyzed by cobalt(II) and bromide ions was monitored among others by measuring the temperature of the reaction system and the pressure of oxygen above the solution as a function of time [409].

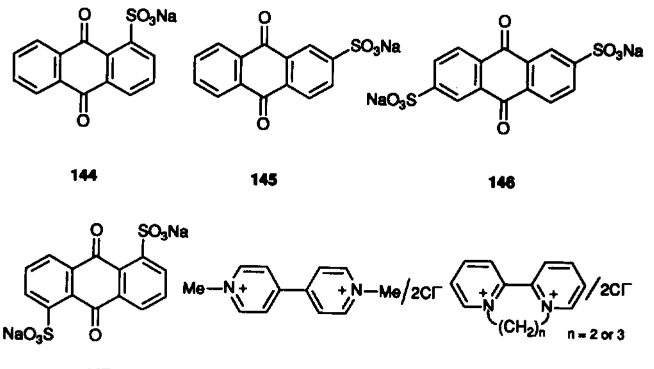
See also [375].

4.2.4. *Miscellaneous oxidations*

The selectivity of the cobalt(II,III) or the vanadium(IV,V)-catalyzed molecular oxygen oxidation of **142** to **143** was induced by using additives such as **144–149**.



142 **143**

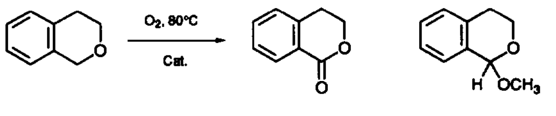


144 **145** **146**

147 **148** **149**

The best result, 96% selectivity, was obtained in the case of vanadium catalyst and **148** as an additive [410].

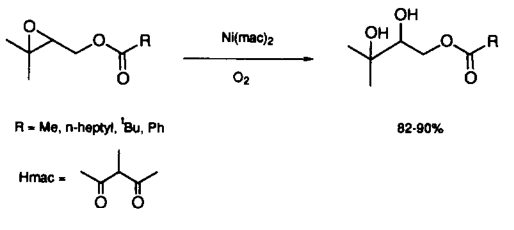
Cobalt(II) chloride-catalyzed oxidation of cyclic ethers with dioxygen in 1,2-dimethoxyethane gave the corresponding lactones in reasonable to excellent yields. *E.g.*:



90% 5%

A free-radical mechanism was proposed involving participation of superoxocobalt [411]. The oxidation of THF and styrene by dioxygen in the presence of $FeCl_2 \cdot 1.5THF$ or $Rh(bpy)(C_2H_4)Cl$ as the catalyst was found to be influenced by CO_2. CO_2 in a 1 : 1 v/v mixture with O_2 enhanced not only the selectivity but increased the rate of the reaction at room temperature and 1 bar pressure. Metal-peroxocarbonate species were suggested to play a key role in these processes [412]. The aerobic oxidation of ethers in the presence of carbon dioxide and catalytic amounts of [Rh(NBD)(PMe$_2$Ph)$_3$][BF$_4$] gave esters and formic acid [413].

A novel method for the preparation of glycerol monoester derivatives by oxidative ring-opening reaction of glycidyl esters with O_2 (6 bar, 100°C) catalyzed by a nickel(II) complex has been reported [414].



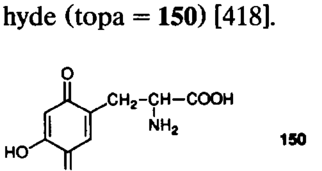
The kinetics of oxidation of CO to CO_2 at 25°C in aqueous solutions of halide complexes of platinum(IV) and $H_7PMo_8V_4O_{40}$ as the catalyst was studied. The catalyst was reoxidized by air [415].

See also [400].

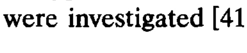
4.3. *Catalytic oxidation of N-containing organic compounds with O_2*

The oxidation of primary benzylamines with dioxygen catalyzed by cobalt(II) bis[3-salicylideneamino)propyl]methylamine was studied. The oxidation gave aldehyde intermediates which reacted with the starting amines to yield the corresponding Schiff bases as the final products [416].

The oxidative carbonylation of amines to carbamates catalyzed by metallomacrocyclic compounds was reported. Salen and porphyrin complexes of cobalt and cobalt, rhodium, ruthenium, respectively, were found to be the most active catalysts (33 mol/mol cat/h) at 180°C and 70 bar CO/O_2 (7% O_2) [417].

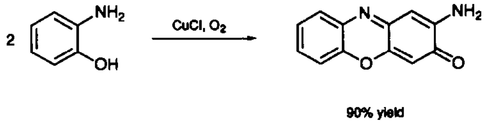


The oxidation of benzylamine with [Cu(DL-topa)(bpy)(H$_2$O)]BF$_4$ · 3H$_2$O in aqueous solution at room temperature under aerobic conditions gave benzaldehyde (topa = **150**) [418].



150

The oxidations of 2-, 3-, and 4-aminophenol with dioxygen at 25°C using different copper compounds were investigated [419]. *E.g.*:



4.4. *Catalytic oxidation of Si-, P-, As-, and S-containing organic compounds with O_2*

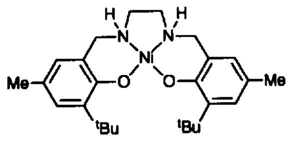
Enantioselective catalysis was demonstrated in the oxidation of DL-cysteine with O_2 in the presence of Fe^{III} and α-alanine enantiomers at varying pH [420].

Triphenylarsinc was selectively and quantitatively oxidized by dioxygen to triphenylarsine oxide at 60–70°C and atmospheric pressure in acetonitrile solution in the presence of iron compounds such as FeX$_3$, FeX$_3$(OAsPh$_3$)$_2$, and [Fe(OAsPh$_3$)$_4$](I$_3$)$_2$ (X = Br, SCN) as the catalyst [421].

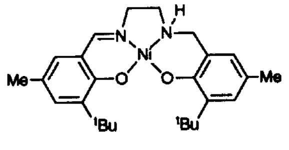
Methyl-*p*-tolyl sulfide was selectively oxidized by dioxygen at 80°C and 7 bar in methanol solution in the presence of various ruthenium-dimethyl sulfoxide complexes as the catalyst precursors [422]. The kinetics of oxidation of dimethyl sulfide with dioxygen to dimethyl sulfoxide catalyzed by [Ru^{III}(EDTA)(H$_2$O)]$^-$ were studied spectrophotometrically [423].

The catalytic activity of cobalt-disulfo-phthalocyanine adsorbed on calcium aluminate was detected during oxidation of dodecylmercaptan to the corresponding disulfide [424]. Cobalt(II) 2,9,16,23-tetrasulfophthalocyanine was found to exhibit a high catalytic activity in the oxygenation of 2-mercaptoethanol to the corresponding disulfide at 25°C in the dark. No increase of activity was observed under irradiation [425]. Cationic polymer colloids were tested as co-catalysts in the autoxidation of 2-mercaptoethanol in the presence of cobalt(II)phthalocyanine tetrasodiumsulfonate. It was found that polymer colloids enhanced the catalytic activity compared with the polymer-free system [426].

Triphenylphosphine was oxygenated to triphenylphosphine oxide at 20°C in acetone solution in the presence of **151**. **151** dehydrogenates during the reaction to **152** [427].



151



152

A new kinetic method for the determination of trace amounts of copper(II) in waste water has been developed based on the Cu^{II}-catalyzed oxidation of water-soluble thiols such as cysteamine, L-cysteine, 2-mercaptoethanol and 2-mercaptopropionic acid [428].

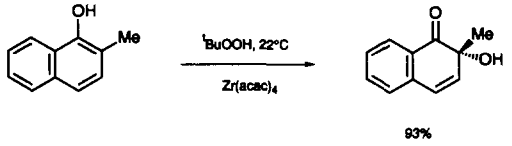
See also [365,373,377,704].

4.5. Catalytic oxidation of organic compounds with organic or inorganic oxidants

4.5.1. Oxidation of hydrocarbons or hydrocarbon groups

Lanthanide porphyrins were found to catalyze the oxidation of styrene with KOCl to a mixture of benzaldehyde, styrene oxide and phenyl acetaldehyde [429].

Ortho-alkylated α- and β-naphthols were oxygenated into the corresponding α-ketols by the reaction with tert-butyl hydroperoxide in the presence of $Ti(O^iPr)_4$, $Zr(acac)_4$ or $[MoO(O_2)]pyHMPA$ [430]. *E.g.*:



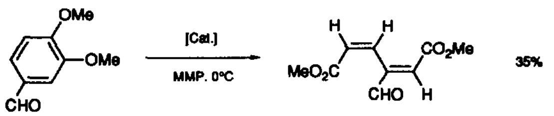
Alkyl hydroperoxides were found as the main products in oxidation of cyclohexane, n-hexane, and 3-methyl-hexane by H_2O_2 catalyzed by Cr^{VI}, V^{V}, Mn^{III}, Pd^{II}, and Fe^{II} at room temperature in acetonitrile solution [431].

Manganese porphyrins adsorbed or intercalated in different mineral matrices were found to catalyze the oxidation of alkene and alkane by PhIO. Mn^{III}[tetrakis-(4-N-methylpyridiniumyl)porphyrin] supported on silica and on montmorillonite were particularly efficient catalysts for heptane and pentane hydroxylation [432]. Sulfonated manganese and iron porphyrin supported on poly(vinylpyridinium) polymers were used as catalysts in cyclooctene epoxidation and adamantane and n-octane hydroxylation with PhIO. In all these oxygenation reactions manganese porphyrins are the better catalysts especially when containing halogen atoms at the pyrrole β-positions [433]. Polyhalogenated Fe^{III} and Mn^{III} porphyrins covalently bound to polymeric supports were found to be active catalysts at 20°C for cyclooctene epoxidation and for the hydroxylation of cyclohexane and heptane by PhIO. The best yields for epoxidation varied from 80 to 100%. The best yields for alkane hydroxylation were 64 and 50%, respectively [434].

Chemical and ^{13}C and ^{2}H NMR spectroscopic evidence was presented, proving that secondary alkyl hydroperoxides are reaction intermediates in the oxidation of saturated hydrocarbons under $GoAgg^{II}$ conditions (ferric chloride, H_2O_2, in pyridine + acetic acid solution). Isolation of cyclohexyl hydroperoxide from a $GoAgg^{III}$ oxidation of cyclohexane ($GoAgg^{II}$ + picolinic acid as catalyst) and the effect of reducing agents (such as thiophenol, benzeneselenal ect.) permit a generalization of the alkyl hydroperoxide intermediacy to the whole family of Gif systems [435]. Mechanistic studies of the iron(III)-catalyzed ketonization of saturated hydrocarbons by tert-butyl hydroperoxide have shown that dioxygen is the precursor of oxygen atom in the products [436].

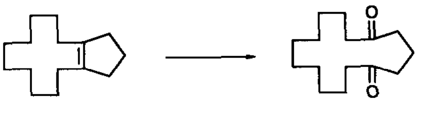
A study of oxidations with hydroperoxides in polar solvents catalyzed by water-soluble iron(III) tetraarylporphyrins was published [437]. Various alkanes (cyclooctane, decalin, tetralin, alkylbenzenes) were oxidized with hydrogen peroxide into ketones and secondary and tertiary alcohols at room temperature using microemulsions containing Fe^{II} or Fe^{III} as the catalysts [438]. The complex $TPPFe^{III}O$ was found to catalyze the oxidation of cyclohexane with PhIO under room temperature and atmospheric pressure. The oxidation products in CH_2Cl_2 and cyclohexane medium were 15 and 62.6%, respectively [439]. The kinetics and products of hydroxylation of cyclohexane and norbornane and the oxidation of their alcohols to ketones were studied using pentafluoroiodosobenzene as the oxidant and highly halogenated iron(III) porphyrins as the catalyst. Experiments with norbornane and tetraexodeuterionorbornane using catalytic amounts of iron(III) tetrakis(2,6-dichlorophenyl)octabromoporphyrin gave a primary isotope effect of 5. This effect and the observed stereochemistry were found to be consistent with free-radical abstraction followed by cage collapse [440].

Selective oxidative cleavage of 1,2-dimethoxyarenes to muconic diesters has been achieved in 30–40% yield by magnesium monoperoxyphthalate (MMP) or H_2O_2 at 0°C in the presence of the water-soluble iron(III) β-sulfonated-tetrakis(pentafluoro-phenyl)porphyrin as the catalyst [441].



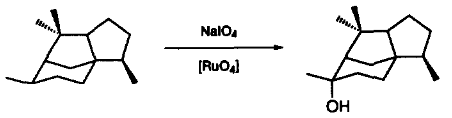
Schiff base complexes of ruthenium(III) were found to catalyze the oxidation of styrene to benzaldehyde by sodium hypochlorite in the presence of a phase transfer agent [442]. Adamantane, cyclooctane, cyclohexane, hexane, and heptane were oxygenated by tert-butylhydroperoxide or hypochlorite at 22°C in the presence of the homogeneous catalysts $K_5[Ru(H_2O)PW_{11}O_{39}]$ and *cis*-$[Ru(H_2O)_2(DMSO)_4](BF_4)_2$ [443]. The $RuCl_3$-catalyzed oxidation of **153** and **155** with $NaIO_4$ afforded **154** and **156** in 65% and 68% yield, respectively [444].

153 **154**



155 **156**

Hydroxylation or ketonization of alkanes was achieved using LiClO or NaClO in the presence of catalytic amounts of Ru^{II} complexes in a biphasic dichloromethane + water system, at room temperature [445]. Cedrane (157) and cedrane derivatives were oxidized with sodium periodate in $MeCN + CCl_4 + H_2O$ at 25°C using *in situ* generated RuO_4 as the catalyst [446]. *E.g.*:



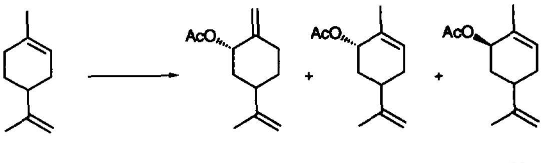
157 69%

A simplified and miniaturized RuO_4-catalyzed oxidation procedure with periodic acid was described for the analysis of both simple organic compounds and biologically derived macromolecules. Tests with regard to the minimum working limit were accomplished down to *ca.* 1 mg [447]. The catalytic ability of ruthenium porphyrins to oxidize alkanes or alkyl alcohols with 2,6-dichloropyridine *N*-oxide was enhanced by the presence of a small amount of HCl or HBr. Thus, methylcyclohexane gave 94% yield of 1-methylcyclohexanol in benzene solution at room temperature in the presence of $Ru(TMP)(O_2)$ (TMP = tetramesitylporphyrinato) as the precatalyst and HBr as the additive [448]. The osmium(VIII)-catalyzed oxidation of cyclohexanone to α-hydroxycyclohexanone and adipic acid by alkaline hexacyanoferrate(III) ions was found to be zeroth-order with respect to $[Fe(CN)_6]^{3-}$ and first-order with respect to $[OH]^-$. The dependence of the pseudo zero-order rate constant on $[Os^{VIII}]$ was given by: $k_0 = a + b[Os^{VIII}]$ [449].

A systematic evaluation of seven iron complexes, $Fe^{II}(PA)_2$, $Fe^{II}(DPA)_2^{2-}$, $FeCl_3$, $Fe^{II}(O_2bpy)_2^{2+}$, $Fe^{II}(OPPh_3)_4^{2+}$, $Fe(MeCN)_4^{2+}$, $Fe^{II}(bpy)_2^{2+}$, and $Co^{II}(bpy)_2^{2+}$ for the ketonization of methylenic carbon, for the monooxygenation of hydrocarbons to alcohols, and for the dioxygenation of arylolefins using H_2O_2 or tert-butyl hydroperoxide has been reported (PA = anion of picolinic acid, DPA = dianion of dipicolinic acid, O_2bpy = 2,2′-bipyridyl 1,1′-dioxide). The reaction efficiencies and product profiles have been determined for five hydrocarbons: cyclohexane, ethylbenzene, toluene, cyclohexene and *cis*-stilbene. In addition, the kinetic isotope effects with cyclohexane and toluene have been measured for each catalytic system [450].

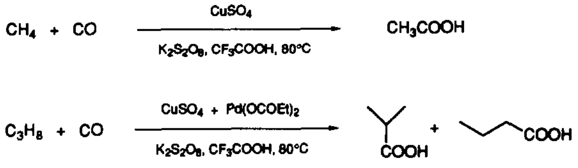
Selective oxidation of terminal olefins to methyl ketones in quantitative yields using montmorillonite silylpropylethylenediamine palladium(II) complex and hydrogenperoxide as reoxidant at 80°C has been described. Turnover numbers as high as 4500 h^{-1} per mole of the catalyst in the epoxidation of 1-octene to 2-octanone has been reported [451].

Acetoxylation of limonene in AcOH at room temperature with $CuCl_2$, $Cu(OAc)_2$, or benzoquinone in the presence of catalytic amounts of Pd^{II} gave **158**, **159**, and **160** in 11:77:12, 5.2:94:0.8, and 49:51:0 ratio, respectively [452].



158 **159** **160**

The formation of acetic acid or butyric acids from methane (40 bar) or propane (10 bar), CO (20 bar) and $K_2S_2O_8$ by $CuSO_4$ and/or $Pd(OCOEt)_2$ catalysts has been reported.

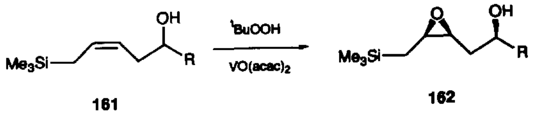


Hydroxylation of phenol, anisole, *m*-cresol, and 1,3-dimethoxybenzene with hydrogen peroxide was catalyzed by cationic complexes of platinum(II) at 85°C. In all cases up to 95% *ortho* selectivity was observed [454].

See also [505,509].

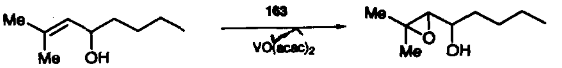
4.5.2. Epoxidation of olefins

Selective epoxidation of **161** with tert-butyl hydroperoxide at −15°C to room temperature in the presence of $VO(acac)_2$ catalyst gave **162** with up to 97:3 *erythro*-selectivity [455].

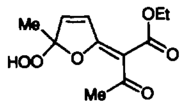


161 **162**

The hydroperoxide **163** was used in a modified Sharpless procedure (VO(acac)$_2$, CH$_2$Cl$_2$, 0–5°C) for the selective epoxidation of trisubstituted allylic alcohols [456]. *E.g.*:

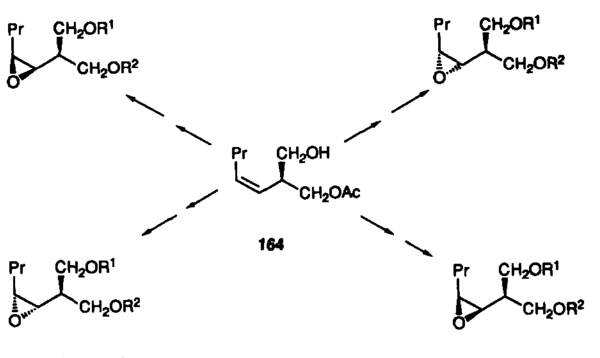


80% yield (erythro/threo = 6/94)



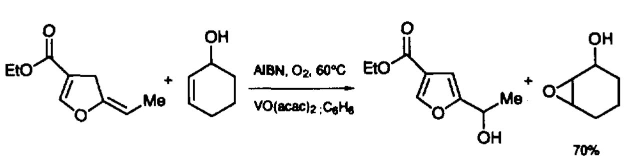
163

All four stereoisomeric *cis*-epoxides were obtained in pure form from a single common (*Z*)-precursor **164** by using VO(acac)$_2$ + ^{t}BuOOH in combination with a protection–deprotection sequence involving the two homoallylic hydroxy groups [457].



R^1 = ^{i}Pr$_3$Si; R^2 = 4-MeOC$_6$H$_4$CH$_2$OCH$_2$

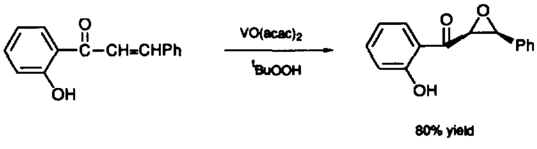
A modified Sharpless procedure for the epoxidation of allylic alcohols and oxidation of sulfides to sulfoxides was reported using VO(acac)$_2$ as the catalyst and *in situ* generated furylhydroperoxides [458]. *E.g.*:



70%

(98:2 = cis:trans)

The *cis*-epoxidation of hydroxychalcones with tert-butyl hydroperoxide in the presence of bis(acetylacetonato)oxovanadium as a catalyst was reported [459]. *E.g.*:

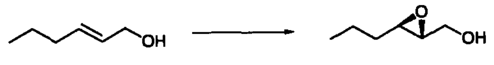


80% yield

The epoxidation of *syn*- and *anti*-5-(tosylamido)-3-hexen-2-ol derivatives was studied using three different epoxidation reagents: *m*-chloroperbenzoic acid, ^{t}BuOOH + VO(acac)$_2$, and ^{t}BuOOH + Ti(O^{i}Pr)$_4$ [460].

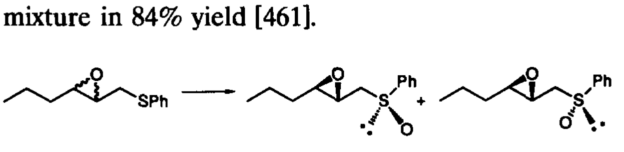
Asymmetric epoxidation of **165** with tert-butyl hydroperoxide/Ti(O^{i}Pr)$_4$ using L-(+)- or D-(−)-diethyl tartrate as the chiral auxiliary gave **166a** or **166b** in 69% or 63% yield, respectively, and > 96% ee.

165 **166 a**



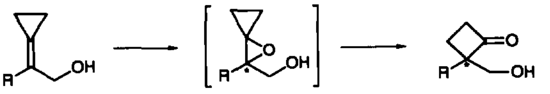
165 **166 b**

The oxidation of racemic **167** with tert-butyl hydroperoxide at −40°C using VO(acac)$_2$ gave the racemic 2,3-epoxy sulfoxides **168 a** and **168 b** as a 1 : 1 mixture in 84% yield [461].



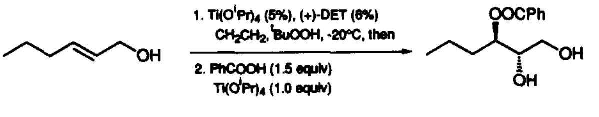
167 **168 a** **168 b**

The Katsuki–Sharpless asymmetric epoxidation (^{t}BuOOH, (−)-diethyl tartrate and (+)-diethyl tartrate or (−)-diisopropyl tartrate and (+)-diisopropyl tartrate, Ti(O^{i}Pr)$_4$, and 3 Å molecular sieves) of cyclopropylidene alcohols **169** and the subsequent rearrangement of the very labile chiral hydroxyoxaspiropentanes **170** gave **171** in good yields and high ee [462].



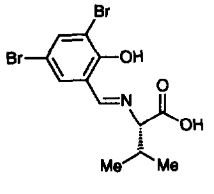
169 **170** **171**

A one pot procedure was used to obtain enantiomerically enriched 1,2-diol benzoates from allylic alcohols combining the Sharpless catalytic asymmetric epoxidation with *in situ* derivatization [463]. *E.g.*:

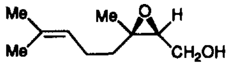


80% isolated yield

The epoxidation of nerol with 1,1-diphenylethyl hydroperoxide in the presence of a 1 : 1 mixture of Ti(O^{i}Pr)$_4$ and **172** (10 mol%) at −40°C gave **173** in 90% yield with 66% ee [464].

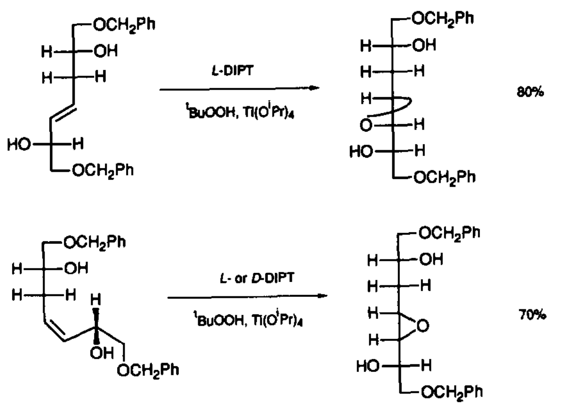


172

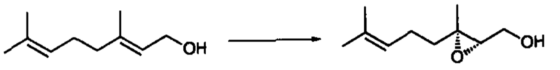


173

The nature of the Katsuki–Sharpless asymmetric epoxidation catalyst was studied by NMR spectroscopy [465]. Asymmetric epoxidation of isomeric chiral allylic-homoallylic diols sharing the central olefinic bond were examined [466]. *E.g.*:

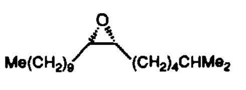


Sharpless epoxidation of geraniol (**174**) in the presence of 1.2 equiv. of (+)-diethyl tartrate afforded the (2*S*,3*S*)-epoxyalcohol **175** in an enantiomeric excess of 94% [467].



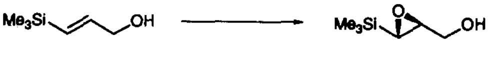
174 **175**

Optically pure **176** was synthesized via asymmetric Sharpless epoxidation of divinylcarbinol in an overall yield of 43.9% [468].



176

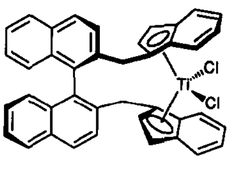
The Sharpless epoxidation of **177** in the presence of 3 mol% of the Ti(O^{i}Pr)$_4$ + L-(+)-diisopropyl tartrate gave 99% ee of **178** [469].



177 **178**

The reaction time of asymmetric epoxidation of allylic alcohol was drastically reduced whereas the enantioselectivity increased when a catalytic amount of CaH_2 and SiO_2 was present in the Sharpless reagent [470]. The Katsuki–Sharpless asymmetric epoxidation of alkenyl ethylene glycol has been used in the syntheses of L-*erythro*- and D-*threo*-sphingosines [471].

The asymmetric catalytic epoxidation of various unfunctionalized alkyl (*e.g.*: *trans*-3-hexene) and aryl alkenes (*e.g.*: styrene) was accomplished using **179** as the catalyst and tert-butyl hydroperoxide as the oxidant. Up to 22% ee and 61 turnovers were observed [472].



179

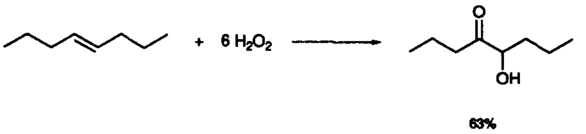
The selective epoxidation of olefins catalyzed by O=Ti(TPP) was investigated. The rates of competitive epoxidations of cycloolefins follows the order: cyclooctene > norbornene > cyclopentene > cycloheptene > cyclohexene. An electron-donating group on the olefin increases the rate of epoxide formation. Addition of pyridine or imidazole decreases substantially the yield of the epoxide. *Cis*-hydroxo(alkylperoxo)tetraphenylporphinatotitanium was suggested to be the active species responsible for epoxidation [473].

The oxidation of cyclohexene with 70% tert-butyl hydroperoxide and CrO_3 catalyst in benzene at 80°C for 3 h afforded the epoxidation product (12.3%), cyclohexenyl peroxide (7.5%), 2-cyclohexenol (2.6%), and 2-cyclohexenone (2.0%). The effect of additives on the yields were investigated [474].

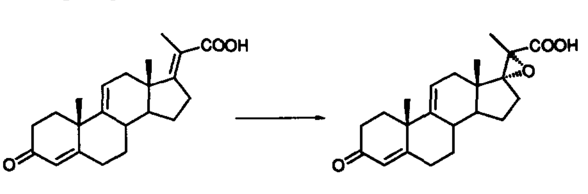
The epoxidation of cyclooctene and 1,5-cyclooctadiene with tert-butyl hydroperoxide using dimeric molybdenum(VI) triketonates as catalysts was investigated at 40 and 80°C in dichloroethane. In comparison with $MoO_2(acac)_2$ the dimeric Mo^{VI} complexes preferentially catalyzed the production of a monoperoxide from the diene [475]. The epoxidation of cyclohexene with aqueous hydrogen peroxide catalyzed by 1,1-dioxomolybdatranic acids $H[MoO_2(OCH_2CH_2)_3N]$ or $H[MoO_2(OCH(CH_3)CH_2)_3N]$ and imidazole was studied. The highest yield of epoxide was obtained when the ratio of imidazole to molybdenum(VI) was 2:1 [476]. Liquid-phase epoxidation of allyl chloride with tert-butyl hydroperoxide was carried out in the presence of various molybdenum complex catalysts in a batch reactor at 53–76°C in 1,12,2-tetrachloroethane solution. $MoO_2(acac)_2$ and $MoCl_5$ were the most active and selective catalysts. The kinetics of epoxidation was studied [477]. The molybdenum complexes of alkanolamines were used as catalysts in the epoxidation of propene with tert-butyl hydroperoxide. The optimum temperature range was found to be 80–100°C leading to 100% conversion of ^{t}BuOOH and 94% selectivity of propene oxide at a molar ratio of propene to ^{t}BuOOH around 1.5 [478].

Mo^{III}(Br$_8$TMP)Cl and Mo^{III}(Cl$_{12}$TMP)Cl catalyze the epoxidation of cyclooctene by 30% hydrogen peroxide in ethyl acetate solution at 70°C [479]. Hydrotalcite pillared with polyoxometalates of molybdenum and tungsten catalyzed the epoxidation of alkenes with hydrogen peroxide in tributyl phosphate at 70°C with significant shape selectivity; epoxidation of 2-hexene was favored over that of cyclohexene [480].

Aliphatic olefins were converted via the corresponding epoxides and *vic*-diols into α-hydroxy ketones with acidic aqueous hydrogen peroxide in the presence of catalytic amounts of peroxotungstophosphate in a biphasic system using chloroform as a solvent [481]. *E.g.*:

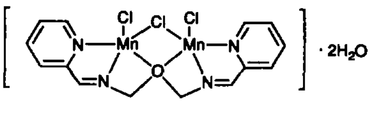


Addition of (meth)acrylic acid to dicyclopentadiene followed by epoxidation with hydrogen peroxide gave epoxy (meth)acrylate [3,4-epoxy-8- or 9-[(meth)acryloyloxy]tricyclo[5.2.1.0^{2,6}]dacene] in good yields using $H_3PW_{12}O_{40}$ as the catalyst [482]. Selective epoxidation of the double bond in the alcohol portion of unsaturated methacrylic esters was achieved by using the system H_2O_2 (20%) + Na_2WO_4 under phase transfer catalysis [483]. Dinorcholenoic acid (**180**) was quantitatively converted to the epoxy acid (**181**) with hydrogen peroxide in pyridine using Na_2WO_4 as the catalyst at 60°C [484].



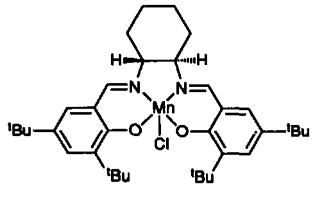
180 **181**

The epoxidations of cyclohexene, norbornene, *cis*- and *trans*-stilbene by iodosylbenzene in the presence of isothiocyanatomanganese(III)-salicylaldehyde *o*-aminophenol as catalyst were studied [485]. Epoxidation of alkenes (norbornene, *cis*-cylooctene, styrene, *trans*-4-octene, and cyclohexene) with iodosylbenzene was studied using mono- and binuclear ruthenium(III)-Schiff base complexes [486] and binuclear manganese (II)-, chromium(III)- and iron(III)-complexes [487] as the catalyst. For example, by the complex **182** 53% epoxide yield was obtained in the case of styrene.



182

The selective epoxidation of norbornene, cyclohexene and *cis*-cyclooctene with PhIO using various Mn^{III} Schiff base complexes as the catalyst was investigated [488]. Higher than 95% ee was achieved in the asymmetric epoxidation of ethyl *cis*-cinnamate using 4-phenylpyridine *N*-oxide oxidant and **183** as the catalyst [489]. The enantioselective epoxidation of *trans*-stilbene with PhIO in the presence of **184** gave the corresponding (1*R*,2*R*)-epoxide in 37% yield and 49% ee [490].



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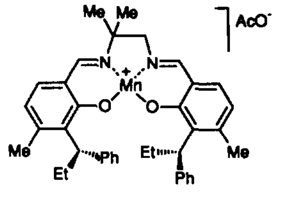
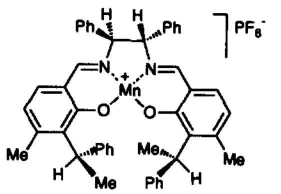


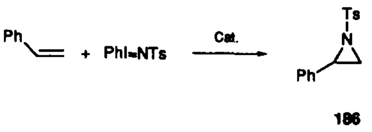
184

The complex **185** was found to catalyze the epoxidation of 2,2-dimethylchromenes with PhIO in acetonitrile at −20°C with high enantioselectivity (86–92% ee) [491].



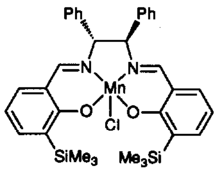
185

The first report of a metal(salen) complex-catalyzed nitrogen transfer from PhI=NTs to olefins was published. In the presence of Mn(salen)Cl as the catalyst in anhydrous dichloromethane styrene gave 46% yield of the corresponding aziridine **186**.



186

The catalytic oxidant in this reaction is presumably a L_nMn=NTs species which transfers its nitrogen to styrene. Chiral manganese salen complexes **187** and **188** catalyzed the aziridination of *Z*-methylstyrene but without asymmetric induction. The same catalysts in asymmetric epoxidation of styrene and *Z*-methylstyrene with PhIO as the oxidant gave 18 and 23% ee, respectively [492].



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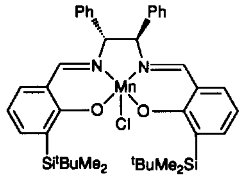


188

cis-Polyisoprene, *trans*-polyisoprene, and *cis*-polybutadiene were transformed to the corresponding polyepoxides with NaOCl and PhIO in the presence of chloro- or acetato-manganese(III) tetraphenylporphyrin as the catalyst. The reaction was monitored by ^{1}H-NMR and infrared spectroscopy [493,494]. The reactivity of oxo-manganese-porphyrin, prepared by the reaction of tetrakis(*p*-chlorophenyl)-porphinatoMnCl with NaOCl, was studied using different kind of olefins [495]. Epoxidation of styrene with sodium hypochlorite in dichloromethane in the presence of various substituted manganese porphyrin complexes as catalysts was investigated. The rate of the reaction and the epoxide selectivity are increased by electron-withdrawing group and *ortho*-substituted manganese porphyrin complexes and by the addition of imidazole [496]. The tetraanion, 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphinatomanganese(III) chloride, bound irreversibly to cationic latexes, was found to be an active catalyst for the epoxidation of alkenes by sodium hypochlorite and potassium peroxymonosulfate in the absence of added organic solvents [497].

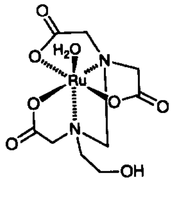
The phase transfer catalysis of PEG-X (X = 200, 400, 1000, 2000) in epoxidation of olefins catalyzed by metal porphyrin with NaOCl in dichloromethane + water biphase system was studied. By anchoring PEG-400 to manganese tetra(*p*-hydroxyphenyl)porphyrin acetate, the catalytic activity and stability of the catalyst were greatly enhanced [498]. The influence of quaternary onium salts, crown ethers and cryptands on olefin epoxidations by aqueous sodium hypochlorite in the presence of Mn^{III}-tetrakis(2,6-dichlorophenyl)porphyrin chloride has been studied. Reaction rates are strongly enhanced by lowering the pH of the aqueous phase from 12.7 to 9.5 [499].

The manganese(III) complex of a new chiral porphyrin, *meso*-tetra($\alpha,\beta\alpha,\beta$-*o*-camphanylamidophenyl) porphyrin was characterized by ^{1}H and ^{13}C NMR spectroscopy and then tested in catalytic chiral epoxidation of styrene using iodosobenzene as the oxidant giving 20% ee [500]. Asymmetric epoxidation of styrene derivatives and vinylnaphthalene by iodosobenzene was achieved by using manganese complexes of the antipodes of *p*-xylylene-strapped porphyrin as catalysts in the presence of imidazole. The optically active epoxides were obtained in 42–58% ee [501,502]. The iron complex of chiral *p*-xylylene-strapped porphyrin catalyzed the asymmetric oxidation of sulfides by iodosobenzene in the presence of imidazole at −43°C [502].

Iron(III) and manganese(III) tetra(2,6-dichlorophenyl)porphyrin bound to surface imidazole and pyridine groups on solid supports were found to be efficient catalysts for the epoxidation of cyclooctene by PhIO [503]. Regioselective monoepoxidations of mainly the less substituted double bond of 1,3-dienes with sodium hypochlorite or iodosobenzene using various ML_n ($M = Mn^{III}$, Fe^{III}; L_n = salens, porphyrins) complexes as the catalysts were reported [504]. Manganese and iron derivatives of Br_8TMP and $Cl_{12}TMP$ were found to be efficient catalysts for olefin epoxidation and alkane hydroxylation by various oxygen atom donors. The kinetic isotope effects of hydroxylation reactions were studied [505].

Iron and manganese derivatives of (*R*)-binaphthalene-linked "twin-coronet" porphyrins were compared as catalysts in asymmetric epoxidation of simple olefins by PhIO or C_6F_5IO. The manganese porphyrin catalyst was found to be better than the iron one, especially for β-substituted styrene derivatives. Up to 70% ee were achieved using C_6F_5IO as the oxidant and 4′-(imidazol-1-yl)acetophenone as axial ligand [506]. Asymmetric epoxidation of various unsubstituted aromatic olefins with PhIO was catalyzed by an iron "binap-capped" porphyrin. The best enantiomeric excess reported was 63% [507].

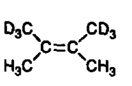
The selectivities and the mechanism of highly efficient epoxidation of olefins with 2,6-disubstituted pyridine *N*-oxides catalyzed by ruthenium porphyrin were studied [508]. The epoxidation of *cis*-stilbene and *trans*-stilbene, and the oxidation of benzylalcohol to benzaldehyde and benzoic acid, sec-phenethyl alcohol to acetophenone, and cyclohexene to 2-cyclohexene-1-one by tert-butyl hydroperoxide catalyzed by **189** was studied [509].



189

The epoxidation of alkenes using the ruthenium(III) chloride/iodosobenzene system were investigated. Addition of pyridine increased the yield and selectivity of the epoxide. The epoxidation of cyclic olefins follows the reactivity order: cyclooctene > norbornene > cyclopentene > cycloheptene > cyclohexene. Spectral studies suggest that oxo ruthenium(V) is the active oxidizing species [510]. Up to 75% yield of 9,10-epoxyoctadecanoic acid was reported in the catalytic epoxidation of oleic acid with $\mathrm{Ru(bpy)_2Cl_2}$ and hydrogen peroxide in tert-butanol at ambient temperature. The rate was found to be first order in hydrogen peroxide and catalyst, and negative first order with respect to the substrate [511]. The rate of epoxidation of cyclohexene with iodosobenzene catalyzed by $\mathrm{Ru^{III}}$-dmg and $\mathrm{Ru^{III}}$-dmg and $\mathrm{Ru^{III}}$-dpg complexes was found to be first order with respect to catalyst concentration and substrate concentration (dmg = dimethylglyoxime, dpg = diphenylglyoxime) [512].

Epoxidation of **190** with $\mathrm{RhCl(PPh_3)_3}$ + cumene hydroperoxide resulted in a 1:1 mixture of *cis*- and *trans*-**191**, while reaction of **190** with $\mathrm{[Fe^{III}(TPP)]Cl/PhIO}$ gave only *cis*-**191** [513].



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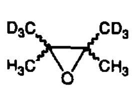


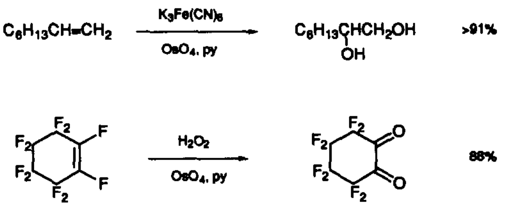
191

The oxidation of cyclohexene by NaOCl in the presence of $\mathrm{[^nHex_4N]_8Cu^{II}P_2W_{17}O_6}$, and $\mathrm{[^nHex_4N]_{16}[Ni^{II}]_4(P_2W_{15}O_{56})_2}$ as the catalysts was reported [514].

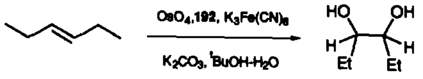
See also [432,433,434,586].

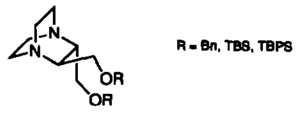
4.5.3. Dihydroxylation of olefins

Oxidation of fluoro olefins with hydrogen peroxide or $\mathrm{K_3Fe(CN)_6}$ in the presence of osmium tetroxide as the catalyst gave in good to yield the corresponding *cis*-diol, ketone or 1,2-diketon [515]. *E.g.*:



Optically active diols in up to 41% ee were obtained in good yields by the osmium tetroxide-catalyzed asymmetric dihydroxylation of olefins in the presence of the chiral ligand **192** [516]. *E.g.*:



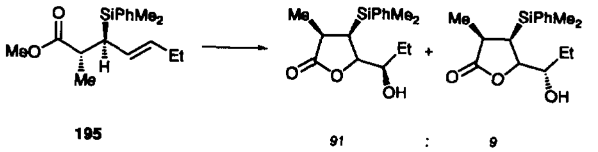


192

Asymmetric dihydroxylation of **193** with $\mathrm{K_3Fe(CN)_6}$ in the presence of catalytic amounts of $\mathrm{K_2OsO_2(OH)_4}$ and dihydroquinidine-9-*O*-(9′-phenanthryl) ether in tert-butyl alcohol + water at 0°C afforded **194** in 60% yield with 97% ee [517]

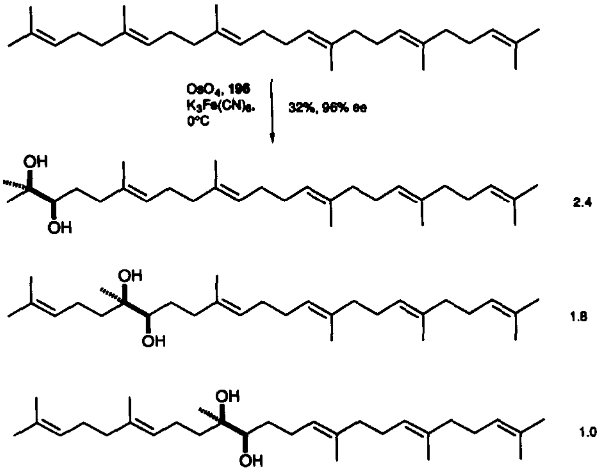
193 **194**

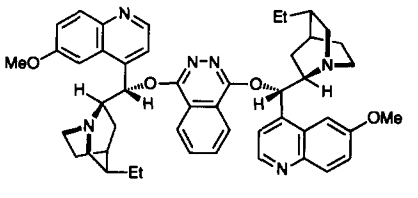
Double asymmetric induction has been used to increase the diastereoselectivity of the dihydroxylation of **195** with $\mathrm{OsO_4}$ + $\mathrm{K_3Fe(CN)_6}$ using the Sharpless asymmetric catalyst dihydroquinidine *p*-chlorobenzoate [518].



195

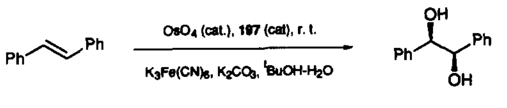
The asymmetric dihydroxylation of squalene with catalytic amounts of osmium tetroxide using $\mathrm{K_3Fe(CN)_6}$ as cooxidant in the presence of the new ligand **196** gave modest regioselectivity but high enantioselectivity [519].



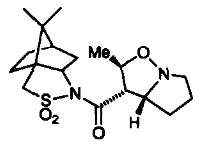


196

Chiral isooxazolidines **197** and **198** were found to be effective chiral ligands for the osmium tetroxide-catalyzed asymmetric dihydroxylation of olefins by $K_3Fe(CN)_6$ [520]. *E.g.*:



99% yield, 73% ee



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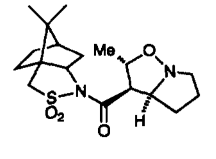
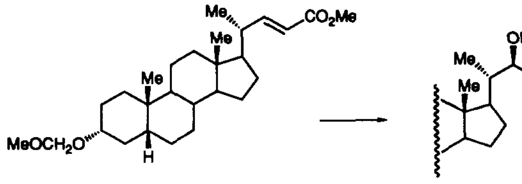


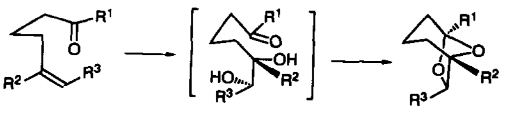
198

High stereoselectivity in asymmetric dihydroxylation of **199** to **200** was achieved using osmium tetroxide + dihydroquinidine *p*-chlorobenzoate + potassium ferricyanide [521].

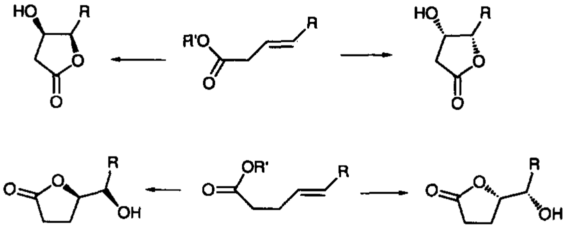


199 **200**

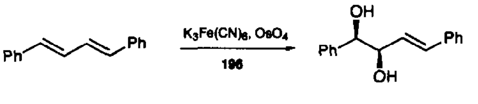
The application of **196** as ligand in the osmium tetroxide-catalyzed asymmetric dihydroxylation of olefins with potassium ferricyanide have led to an improvement of the procedure. Enantiomeric excesses of the resulting diols were up to 99.5% in the case of *trans*-$R^1CH{=}CHR^2$ type olefins [522]. Adaption of this improved methodology was used in the synthesis of the carbon–oxygen framework of (−)-frontalin and brevicomin in 60–70% ee [523].



Hydroxy γ-lactones were prepared highly enantioselectively (92–99% ee) using osmium-tetroxide-catalyzed asymmetric dihydroxylation of β,γ- and γ,δ-unsaturated esters with potassium ferricyanide in the presence of the corresponding 1,4-bis-dihydroquinidine-phthalazine ligand **196** [524,525].



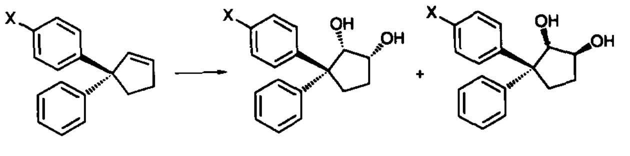
Up to 80% ee in catalytic asymmetric dihydroxylation of *cis*-disubstituted olefins were achieved by using the carbamate ligand (9-*O*-indolinylcarbamoyl)-dihydroquinidine in combination with osmium tetroxide and potassium ferricyanide in tert-butyl alcohol + water at 0°C [526]. High yields and high enantiomeric excess of ene diols were obtained in the osmium tetroxide-catalyzed dihydroxylation of dienes using 3 molar equiv. of potassium ferricyanide as the stoichiometric oxidant and **196** as the ligand [527]. *E.g.*:



84% yield, ≥99% ee

α-Hydroxy ketones were isolated in 68–95% yields and with good to excellent enantiomeric excesses by the osmium-catalyzed asymmetric dihydroxylation of the corresponding enol ethers [528].

The formation of glycosyl glycerol derivatives from allyl D-glucopyranoside by osmium tetroxide-catalyzed dihydroxylation with *N*-methyl morpholine *N*-oxide in aqueous acetone at 0°C was reported [529]. It was shown that in the osmium tetroxide-catalyzed dihydroxylation of 3,3-diarylcyclopentenes **201** with triethylamine *N*-oxide the diastereoselectivity is controlled by stereoelectronic factors.



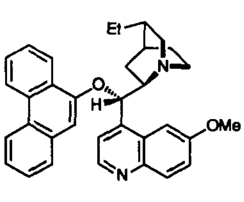
201 trans-**202** cis-**202**

$X = NO_2, Cl, Br, OMe, \overset{+}{N}Me_3$

The *cis* : *trans* ratios (diol relative to the substituted arene) in **202** varied from 70:30 to 36:64, and a

Hammett plot of log(*cis* : *trans*) *vs.* the σ_p parameter gave a linear relationship with a slope of 0.46 [530].

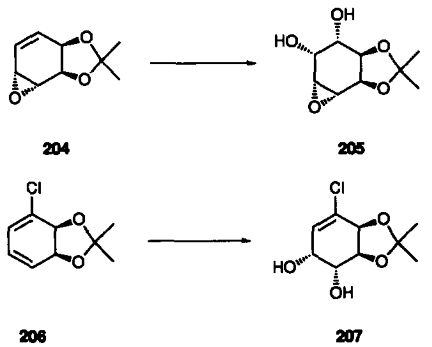
The osmium-catalyzed asymmetric dihydroxylations of 1,3-enynes using **196** and **203** as chiral ligands were studied. Terminal olefins gave 38–79% ee and *trans*-disubstituted olefins gave 73–97% ee [531].



203

The use of dihydroquinidine and dihydroquinine on a polystyrene support in the osmium tetroxide-catalyzed asymmetric dihydroxylation of alkenes (*trans*-stilbene, styrene, methyl cinnamate and octenes) by *N*-methyl morpholine *N*-oxide furnished diols in high yields (79–87%) and good enantioselectivity (22–85% ee) [532].

Catalytic osmylation of **204** and **206** using osmium tetroxide, *N*-methyl morpholine *N*-oxide in acetone + water gave the corresponding diol **205** and **207** in 92% and 65% yield, respectively [533].



204 **205** **206** **207**

The 22*R*,23*R*-homobrassinosteroid analogs were obtained in good yield from the corresponding precursor with a 22*E*-double bond by osmium tetroxide-catalyzed asymmetric dihydroxylation using trimethylamie *N*-oxide as reoxidant and dihydroquinidine 9-*O*-(9′-phenanthryl)ether as chiral agent [534].

Glycosyl-*myo*-inositols were obtained in high yield by the osmium tetroxide-catalyzed *cis*-dihydroxylation of 4-*O*-glycosyl-1-*O*-acetyl-conduritol B derivatives with trimethylamie *N*-oxide [535].

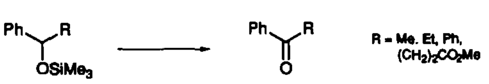
The catalytic hydroxylation of 1-chloro-2-propene, 1-chloro-2-butene, and cinnamyl chloride was carried out with ascorbic acid and poly(methyl methacrylate)-supported copper(I) ion system at pH 4.0 under an argon atmosphere at 30°C. The observed turnover values were about 50 times higher than in the absence of the polymeric support. This was explained in term of an increase in the concentration of reaction substrate by hydrophobic micro atmosphere on the surface of the support [536].

4.5.4. Oxidation of O-containing functional groups

Stirring PhCOCPh(OH)R (R = Me, Me_2CH, Bu, $PhCH_2$, 4-$ClC_6H_4CH_2$) with $NaBrO_3$ in acetonitrile + water in the presence of ceric ammonium nitrate as the catalyst at 40–50°C gave PhCOR in 71–86% yield [537].

Vanadyl pyrophosphate was found to be extremely effective for oxidative dehydrogenation of isobutyric acid and for oxidation of methacrolein to methacrylic acid [538]. The oxidation reactions of chromotropic acid derivatives by potassium bromate in the presence of vanadium(V) were studied. Spectrophotometric, polarographic and ^1H NMR methods were used to observe the oxidation products [539].

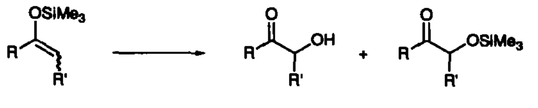
The oxidation of **208** with aqueous 70% tert-butyl hydroperoxide and catalytic amounts of a mixture of Ph_3SiOH and CrO_3 at room temperature gave **209** in 93–99% yield [540].



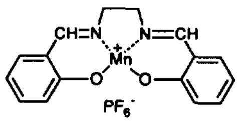
208 **209**

Aromatic aldehydes were oxidized under mild conditions to the corresponding carboxylic acids in good yields using a manganese(III) porphyrin complex + sodium hypochlorite system [541].

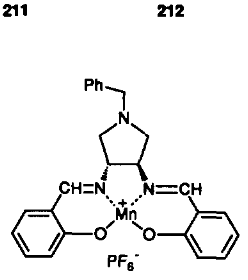
The oxidation of ketone silyl enol ethers **210** with iodosobenzene at 25°C in acetonitrile in the presence of **213** or **214** as the catalyst gave α-oxygenated products **211** and **212** in good to excellent yields. *E.g.*:



210 **211** **212**

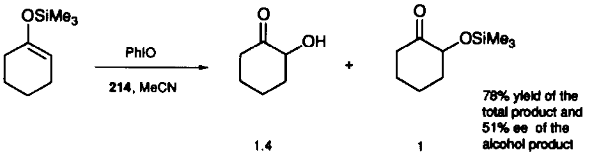


213

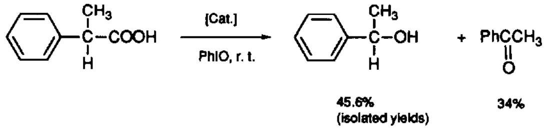


214

Asymmetric induction using **214** as the catalyst varied from 14 to 62% ee [542]. *E.g.*:



α-Aryl carboxylic acids and α,α,α-trisubstituted acetic acids were oxidized to the corresponding alcohol and carbonyl derivatives by an iodosylbenzene-*meso*-tetrakis(pentafluorophenyl)porphyrin iron chloride catalyst system [543]. *E.g.*:



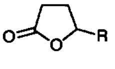
The hydrogen ion dependence in the oxidation of L-ascorbic acid by hexacyanoferrate(III) in a water + alcohol mixture was studied [544].

The oxidation of benzoin to benzil with *p*-benzoquinone or air and of *p*-substituted benzhydrol to benzophenone with air was effectively catalyzed by $[Fe^{II}(SPh)_4]^{2-}$ and $[Fe^{II}(SePh)_4]^{2-}$ at 25°C and 1 bar [545]. The oxidation of benzoin by *p*-benzoquinone in the presence of a polymer supported ferredoxin model complex $[^nBu_4N]_2[Fe_4S_4(S\text{-}^tBu)_3(S\text{-}PSt)]$ (S-PSt = crosslinked poly(styrene) *p*-methylene-thiolate) was investigated [546].

The rates of oxidation of D-mannitol to D-mannose by Tl^{III} with Ru^{II} as catalyst were measured in acetic acid medium. The reaction is first order in $[Tl^{III}]$, fractional order each in [substrate] and [catalyst] [547].

A novel synthesis of α-keto acid derivatives via oxidative dehydrogenation of α-hydroxy acid derivatives with tert-butyl hydroperoxide at room temperature catalyzed by $RuCl_2(PPh_3)_3$, $RuCl_3$, and Ru + C was reported. The procedures are applicable to aromatic, heteroaromatic, aliphatic, and olefinic α-hydroxy esters and nitriles without side reactions [548].

Mixtures of $Me(CH_2)_7OH$ and $Me(CH_2)_3CH(OH)(CH_2)_2Me$ were oxidized by 4-methylmorpholine *N*-oxide in the presence of tetra-n-propylammonium perruthenate to $Me(CH_2)_6CHO$ and $Me(CH_2)_3CO(CH_2)_2Me$ in 85 and 15% yield, respectively. Using this catalyst $HO(CH_2)_3CH(OH)R$ [R = Pr, $(CH_2)_6Me$, Ph] was selectively oxidized to lactone **215** [549].

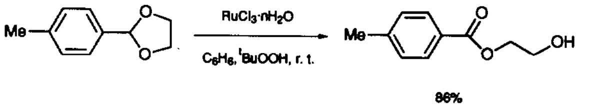


215

The kinetics of oxidation of three aldoses (glucose, mannose, and galactose) to the corresponding aldonic acids by *N*-bromoacetamide in the presence of an alkaline solution of ruthenium tetroxide as catalyst and $Hg(OAc)_2$ as co-catalyst and a scavenger for bromide were investigated. The reaction is zero order with respect to aldose and hydroxyl ion, first order with respect to the oxidizing agent and ruthenium tetroxide at low concentrations [550]. The kinetics and isotope effects of the ruthenium(VI)-catalyzed oxidation of benzyl alcohol and its monosubstituted analogs by hexacyanoferrate(III) were studied [551].

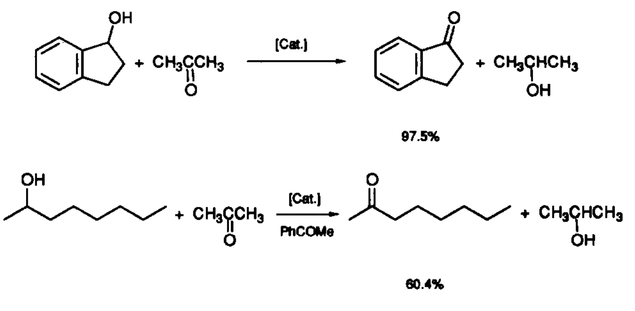
Purine and pyrimidine nucleosides were oxidized to the corresponding 5′-carboxylic acids using potassium persulfate as the reoxidant and ruthenium trichloride as the catalyst precursor under basic conditions at room temperature [552].

Glycol monoesters were prepared from the corresponding cyclic acetals by ruthenium(III)-catalyzed oxidation using tert-butyl hydroperoxide as the oxidant [553]. *E.g.*:



The kinetics of the ruthenium(III)-catalyzed oxidation of cyclohexanol by bromamine-T in hydrochloric acid were studied. The reaction was found to be first order with respect to oxidant, cyclohexanol, Ru^{III}, and hydrogen ion [554]. The kinetics of oxidation of 2-propanol and 1-propanol by hexacyanoferrate(III), diperiodocuprate(III), periodate, and chloramine T in aqueous alkali solution in the presence of sodium ruthenate as the catalyst were investigated [555]. Kinetics of the ruthenium(III) chloride-catalyzed oxidation of 2-butanol by hexacyanoferrate(III) in alkaline medium were studied by UV spectrophotometry. The rate is zero-order with respect to the oxidant and first-order with respect to the alcohol at low concentrations. The activation parameters were obtained [556].

Secondary alcohols were readily converted to ketones at 56°C under dinitrogen by acetone in the presence of a catalytic amount of $RuCl_2(PPh_3)_3$. In some cases the reaction was co-catalyzed by acetophenone. *E.g.*:

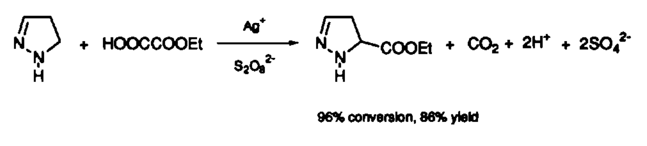


Turnover rates as high as 1900/h were achieved in the case of the most reactive alcohols of five-membered rings [557].

Ruthenium(II) and ruthenium(III) complexes with *O,O*-donor ligands were found to be effective catalysts for the oxidation of *p*-methoxybenzyl alcohol to *p*-methoxybenzaldehyde in the presence of *N*-methylmorpholine-*N*-oxide as co-oxidant [558]. Ruthenium (III) complexes, $[Ru^{III}X_2(AsPh_3)_2HL]$ ($X = Cl$, Br; H_2L = Schiff bases from 2,3-dihydroxybenzaldehyde and aniline or its *ortho*- and *para*-substituted derivatives) were found to catalyze the oxidation of primary alcohols to aldehydes, secondary alcohols to ketones, and 3,5-di(tert-butyl)catechol to the corresponding *o*-benzoquinone in the presence of *N*-methyl-morpholine *N*-oxide as co-oxidant [559]. Complexes of 2-hydroxyl-1,4-naphthoquinone with uranium, molybdenum, ruthenium and osmium were tested for the oxidation of primary alcohols to aldehydes and of secondary alcohols to ketones in the presence of *N*-methyl-morpholine *N*-oxide as co-oxidant [560].

The cobalt complex of tetrakis(3-methoxy-4-hydroxy-4-hydroxyphenyl)porphyrin has been used as catalyst in oxidation of quinhydrone and butyl mercaptan [561]. The kinetics of oxidation of indigo carmine in Co^{II}- and Ni^{II}-citric acid + H_2O_2 solutions at pH 9–11 were studied. A general expression for the rate constant of oxidation is derived [562].

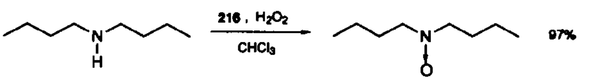
Alkoxycarbonyl radicals were generated by silver(I)-catalyzed oxidative decarboxylation of oxalic acid monoester by $S_2O_8^{2-}$. They were utilized for the alkoxycarbonylation of heteroaromatic bases with good yields [563]. *E.g.*:

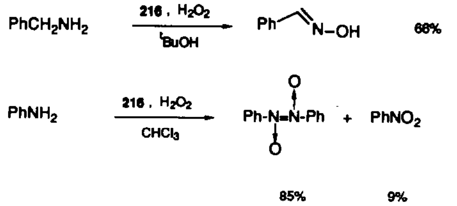


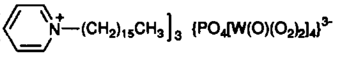
See also [440,448,509].

4.5.5. Oxidation of N-containing organic compounds

Peroxotungstophosphate **216** was found to catalyze the oxidation of amines with 35% hydrogen peroxide under biphasic or homogeneous condition. Thus primary and secondary amines were oxidized to oximes and nitrones, respectively. Aromatic amines afforded the corresponding nitroso compounds and/or nitrobenzenes [564]. *E.g.*:







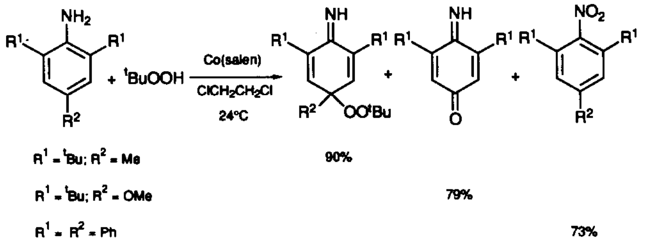
216

The oxidation of $PhCH_2O_2C$ + histidine-OMe with $RuCl_3 + NaIO_4$ in acetonitrile + $CCl_4 + H_2O$ gave asparagine and aspartic acid derivatives in 22 and 25% yields, respectively [565].

The kinetics of the osmium(VIII)-catalyzed oxidation of 2-aminoethanol and 3-aminopropanol by hexacyanoferrate(III) in alkaline medium were studied spectrophotometrically. The reaction was found to be first-order each in oxidant, alkali and catalyst. Zero-order was found with respect to the substrate concentration. Hexacyanoferrate(II) has an inhibiting effect on the rate of the reaction [566]. The kinetics and mechanism of oxidation of uric acid by chloramine-T were studied in the presence of osmium(VIII) in alkaline medium. A redox cycle involving Os^{VIII}/Os^{VI} has been suggested [567].

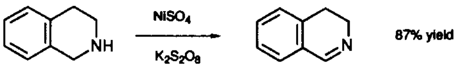
A simple and accurate (to ± 0.26%) titrimetric method for determination of salicyloylhydrazine using hexacyanoferrate(III) as reagent, *N*-phenylanthranilic acid as an indicator and osmium tetroxide as the catalyst was reported [568].

Oxidation of 2,4,6-trisubstituted (preferentially 2,6-di-tert-butylated) anilines with tert-butylhydroperoxide in the presence of Co(salen) as the catalyst gave 4-tert-butylperoxy-2,5-cyclohexadien-1-imine and nitrobenzene derivatives. The relative ratio of the products depends on the nature of the substituents in the substrate [569]. *E.g.*:



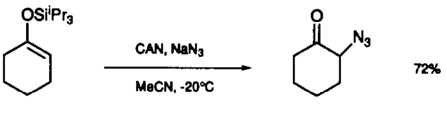
The kinetics of Rh^{III}-catalyzed oxidation of glutamic acid by hexacyanoferrate(III) in alkaline medium were studied. The reaction showed zero-order dependence on oxidant and hydroxyl ion, and first-order dependence with respect to glutamic acid and Rh^{III} [570].

In connection with the toxicity and carcinogenicity of nickel it was found that the effectiveness of conversion of the 2′-deoxyguanosine residues in calf thymus DNA to 8-hydroxy-2′-deoxyguanosine by treating the DNA with hydrogen peroxide in the presence of $NiCl_2$ was enhanced by the addition of L-histidine, which forms a Ni^{II}-histidine complex [571]. The catalytic system consisting of $NiSO_4$ and $K_2S_2O_8$ was found to be effective for the oxidation of secondary amines to imines at room temperature [572]. *E.g.*:



4.5.6. *Oxidation of Si-, P-, S-, Se-, and halogen-containing organic compounds*

α-Azido ketones were obtained in 50–80% isolated yield by treatment of triisopropyl enol ethers with ceric ammonium nitrate (CAN) and sodium azide at −20°C [573]. *E.g.*:

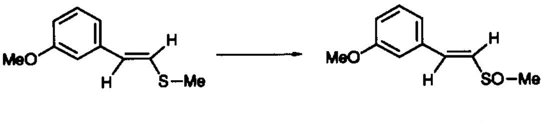


Catalytic asymmetric oxidation of aryl methyl sulfides using $Ti(O^iPr)_4$ as a catalyst, tert-butyl hydroperoxide as an oxidant and *R*-(+)-binaphthol as a chiral auxiliary gave high chemical yield and up to 73% ee of the corresponding sulfoxides [574]. Compound **217** have been obtained in high diastereomeric excess (> 99 : 1) and enantiomeric excess (up to 94%) by enantioselective oxidation of the corresponding dithiolanes using $Ti(O^iPr)_4$, (+)-diethyl tartrate and tert-butyl hydroperoxide in dichloroethane at −20°C [575].

R = Me, Et; R_2 = $-(CH_2)_4-$

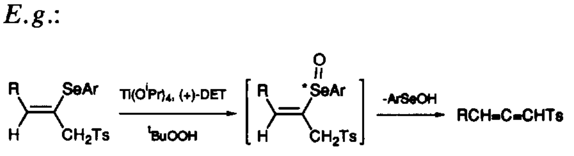
217

Prochiral vinyl sulfides were oxidized to the corresponding (*S*)-vinyl sulfoxides with cumene hydroperoxide in the presence of a stoichiometric amount of water-modified $Ti(O^iPr)_4$ + (*S*,*S*)-(−)-diethyl tartrate + H_2O = 1 : 2 : 1 reagent in dichloromethane at −20°C [576]. *E.g.*:



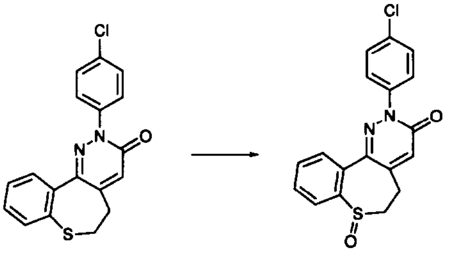
41% yield; 95% ee (*S*)

The Sharpless oxidation of *o*-nitrophenyl vinyl selenides gave chiral allenes *via* asymmetric selenoxide elimination in moderate enantiomeric excess (up to 21%) and in a good chemical yield (up to 86%) [577]. *E.g.*:



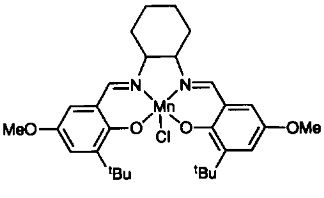
R = ^nPr, n-C_7H_{15}, Cl
Ar = o-$NO_2C_6H_4$, Ph

Vanadium pillared montmorillonite catalyst afforded up to 99% yield of sulfoxides at room temperature in the liquid phase oxidation of sulfides by tert-butyl hydroperoxide. In the presence of (+)-diethyl tartrate chiral auxiliary at −20°C 16–25% ee was achieved [578]. Both enantiomers of **219** were synthesized in high yields by asymmetric oxidation of the synthetic precursor **218** using modified Sharpless reagent. Cumene hydroperoxide gave the highest optical and chemical yields [579].



218 **219**

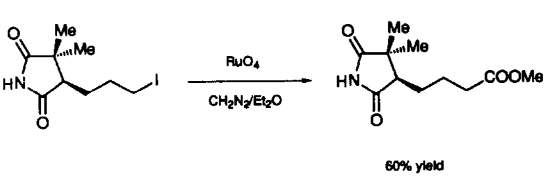
Asymmetric oxidation of prochiral sulfides with H_2O_2 catalyzed by optically active $(salen)Mn^{III}$ complexes was studied. Using (*R*,*R*)-**220** or (*S*,*S*)-**220** as the catalyst 84–95% chemical yield of sulfoxides and 34–68% ee were achieved [580].



220

Iron porphyrins bearing *S*-naphthyl-propionic amide at the *meso* position were found to catalyze the asymmetric oxidation of sulfides with PhIO and tert-butyl hydroperoxide, and 5–15% ee was reported [581]. Asymmetric oxidation of aryl sulfides by PhIO was achieved using novel chiral iron porphyrin catalysts, affording the corresponding sulfoxides in 18–71% ee [582].

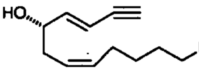
A procedure for the oxidation of sulfides to sulfones using ruthenium tetroxide as catalyst and periodic acid as stoichiometric oxidant in a biphasic system (CCl_4, MeCN, H_2O) was reported [583]. A mild and efficient oxidation of primary alkyl iodides to carboxylic acids were achieved with $RuCl_3 + H_5IO_6$ in $MeCN + CCl_4 + H_2O$ and $CH_2N_2 + Et_2O$ in one step [584]. *E.g.*:



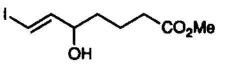
See also [236,458,461,502,561].

4.5.7. *Kinetic resolution by asymmetric oxidation*

Compound **221** and **222** were obtained by the Sharpless kinetic resolution of the racemates [585].

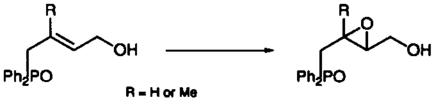


221



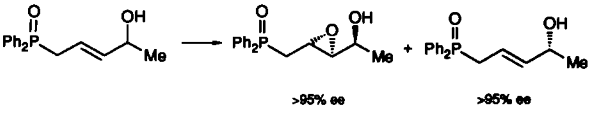
222

Asymmetric synthesis of epoxides **224** from allylic phosphine oxides **223** using the enantio- and diastereoselective Sharpless epoxidation (2 equiv. ${}^tBuOOH$, 1 equiv. $Ti(O^iPr)_4$, 1.2 equiv. L-(+)-DET, 4 Å mol sieves, CH_2Cl_2, −16°C) afforded 76–91% yield and 82–96% ee.

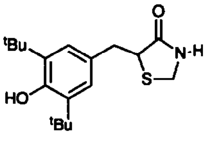


223 **224**

When secondary allylic alcohols bearing a chiral center d to phosphorus were epoxidized using only 0.5 equiv. of hydroperoxide and L-(+)-diisopropyl tartrate a kinetic resolution was observed, allowing both remaining starting material and product epoxy alcohol to be isolated in good ee [586]. *E.g.*:



The kinetic resolution of racemic **225** by enantioselective sulfoxide formation using (+)-diisopropyl tartrate, $Ti(O^iPr)_4$, tert-butyl hydroperoxide, 4 Å molecular sieves in CH_2Cl_2 at −20°C gave (−)-**225** with 66% ee [587].



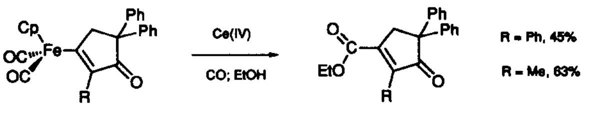
225

An enantiomeric excess of nearly 20% of the resolved hydroperoxide has been observed in kinetic resolution of 1-methyl-1-phenylpropyl hydroperoxide via catalytic Sharpless epoxidation with cinnamyl alcohol or α-phenylcinnamyl alcohol [588].

4.6. *Stoichiometric oxidation of organic compounds with high valent transition metal complexes*

4.6.1. *Oxidation of hydrocarbons or hydrocarbon groups*

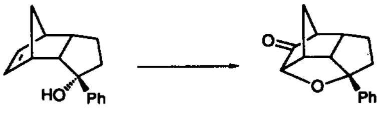
The oxidation of 4-methylcyclohexene and 2,3-dimethylcyclohexanol to acyclic dicarboxylic acids by cerium(IV) ions were studied by kinetic, spectral, and MO methods and by product analysis [589]. The oxidative carbonylation of **226** using ceric ammonium nitrate afforded **227** in moderate to good yields [590].



226 **227**

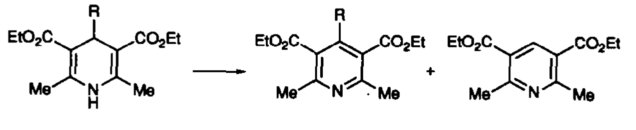
Kinetic and product studies of oxidation of methyl cyclohexenes with cerium(IV) in solutions of perchloric acid have shown that the methyl group in 1-methylcyclohexene was oxidized to CO_2 whereas that of 3-methylcyclohexene remained intact [591]. The kinetics of oxidation of *m*-xylene to *m*-methylbenzyl alcohol and *m*-tolualdehyde by ceric sulfate in sulfuric acid solution were studied [592]. The kinetics of oxidation of 4-methylanisole → anise alcohol → anisaldehyde → anisic acid by ceric sulfate have been studied by absorption spectroscopy [593].

Pyridinium chlorochromate oxidation of **228** afforded **229** in 70% yield [594].



228 **229**

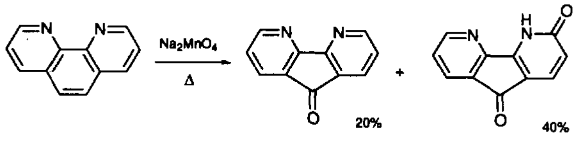
Oxidation of **230** under neutral conditions using pyridinium chlorochromate adsorbed on a solid support such as alumina, silica gel, and montmorillonite, gave **231** (if R = H, Et, Pr, Ph, substituted Ph, 2-furyl, 2-thienyl) or **232** (if R = $CHMe_2$, $CHPh_2$, or CH_2Ph) as the sole product [595].



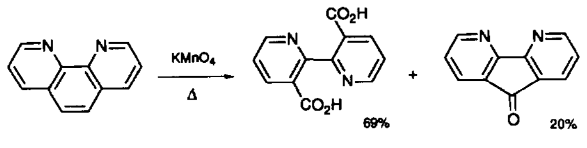
230 **231** **232**

The kinetics and mechanism of oxidation of malonic acid by chromium(VI) in aqueous perchlorate medium were studied [596]. The kinetics of oxidation of 3-alkyl- and 3,5-dimethyl-substituted 2,6-diphenylpiperidin-4-ones by pyridinium fluorochromate in aqueous acetic acid medium in the presence of perchloric acid were investigated. 3-Hydroxy-substituted piperidin-4-ones and substituted pyrrolidine-3-carboxylic acids were found to be the major products of oxidation. The reactions are first-order each in [oxidant] and [substrate], and show a primary isotope effect, $k_H/k_D = 4.2$. The order of reactivity was found to be: 3-Et > 3-Me > 3-^{i}Pr > 3-H > 3,5-di-Me [597]. The kinetics of oxidation of methoxytoluenes by quinolinium dichromate in acid medium were studied. The rate of the reaction is first-order in each substrate, oxidant, and acid. A kinetic isotope effect, $k_H/k_D = 6.2$, was observed [598].

Dibenzo[*a*]pyrenes and anthanthrene were oxidized with manganese(III) acetate in AcOH + benzene at 40°C to monoacetoxy and diacetoxy derivatives [599]. The oxidation of 1,10-phenanthroline with tetraoxomanganate(VI) gave **233** and **234**. Using tetraoxomanganate(VII) gave **235** as the main product [600].

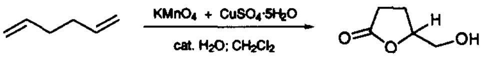


233 **234**

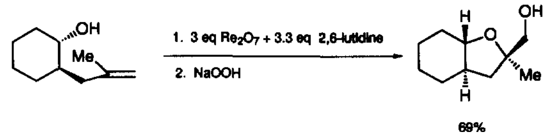


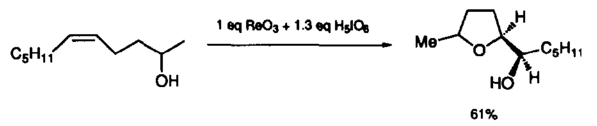
235 **233**

Heterogeneous permanganate oxidation of 1,5-dienes was found to lead to the formation of the corresponding butanolides [601]. *E.g.*:

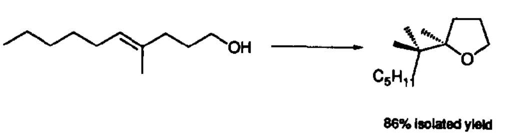


The oxidation of 5-hydroxyalkenes with rhenium oxide provided substituted 2-hydroxymethyl-tetrahydrofurans [602,603]. *E.g.*:



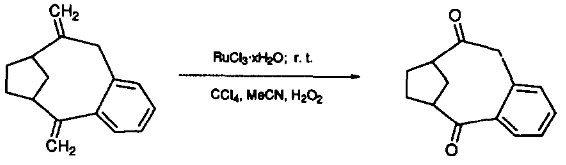


The oxidative cyclization of 5-hydroxyalkenes with rhenium(VII) oxide at room temperature gave 2-hydroxymethyltetrahydrofurans in good yields [604]. *E.g.*:



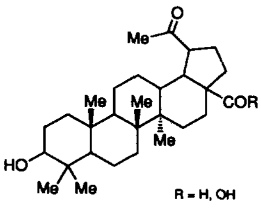
The oxidation of polycyclic aromatic hydrocarbons by oxoferryl porphyrin cation radicals was described [605]. The kinetics of oxidation of 3-methylascorbic acid with aqueous iron(III) were studied by stopped-flow. Two parallel pathways, whose contributions depend on the $[Fe^{2+}]$, were identified. One pathway has a $[Fe^{2+}]^{-1}$ dependence and has an irreversible step prior to the transfer of the second electron. The other pathway, with an $[Fe^{2+}]^{-2}$ dependence, is analogous to that found previously for 1,2-dihydroxybenzoic acid [606].

The ruthenium tetroxide oxidation of **236** under mild conditions gave **237** in 65% yield [607].



236 **237**

Compounds **238**, **239**, and **240** were obtained in oxidations of betulin, dihydrobetulin, and 3*β*,28-dihydroxy-18-lupene, respectively by ruthenium tetroxide [608].



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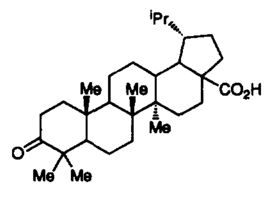

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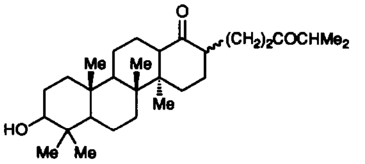


240

The O atom transfer reactions from K[Ru^V=O(EDTA)] and K[Ru^V=O(PDTA)] (PDTA = propylenediaminetetraacetate) to unsaturated and saturated hydrocarbons were studies spectrophotometrically in the temperature range 30–50°C [609]. The oxidation of *N,N′*-diacetyl and -dibenzyl piperazine by ruthenium tetroxide were studied. The two adjacent methylene groups were preferentially oxidized [610]. The kinetics of oxidation of carbon–hydrogen bonds and alkenes by *trans*-dioxoruthenium(VI) porphyrins were investigated. The complexes were selective towards tertiary C–H bonds in saturated alkenes but were almost inactive towards secondary C–H bonds. The major organic products of the oxidation of alkenes in CH_2Cl_2 + MeOH mixtures were epoxides [611]. Reactivity, kinetic isotope effect and activation parameters of the ruthenium tetroxide-mediated oxidation of saturated hydrocarbons were studied [612]. The kinetics of oxidation of aromatic hydrocarbons and tetrahydrofuran by *trans*-dioxoruthenium(VI) complexes were investigated. In acetonitrile the second-order rate constants follow the order: toluene < ethylbenzene < cumene. Large kinetic isotope effects (up to 20) were found. A hydrogen-atom abstraction mechanism is suggested [613].

The product distribution and kinetics of the oxidation of 2-cyclohexenol and 2-cyclohexenol-1-*d* by $PdCl_4^{2-}$ in aqueous solution were investigated [614]. The formation of 1,1- and 1,2-addition products during ethylene oxidation by $Pd(NO_n)_mCl_{2-m}L_2$ ($n = 2$, 3; $m = 0$, 1, 2; L = CD_3CN) in chloroform + acetic acid solution was studied with ^{1}H NMR [615].

The oxidation of ethers, alcohols, esters, and alkanes such as ethane and propane by K_2PtCl_4 or by the combined use of K_2PtCl_4 and Pt/O_2 in aqueous medium has been studied. Pt^{II} was found to oxidize ethane selectively to a mixture of ethanol and ethylene glycol at 122°C. Further oxidation occurred only in the presence of metallic platinum. The oxidation of ethyl ether by Pt^{II} gave at 90°C a mixture of ethylene glycol, glycolic acid, chloroacetic acid and acetic acid in 1:2:1.5:2 ratio with a 20.1% combined yield relative to the oxidant [616]. Water-soluble organic compounds such as *p*-toluenesulfonic acid and ethanol were hydroxylated by aqueous solutions of chloroplatinum(II) and chloroplatinum(IV) salts. The alcohols were further oxidized to the corresponding aldehydes [617].

Tetrakis(pyridine)silver(II) peroxidisulfate has been found to be a mild oxidizing agent for aromatic aldehydes to carboxylic acids, benzylic alcohols to carbonyl compounds, aromatic thiols and allylaryl thioethers to arylsulfonic acids in acetonitrile at room temperature or at reflux temperature [618].

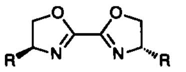
See also [685].

4.6.2. Epoxidation and dihydroxylation of olefins

The kinetics of the oxidation of 1-octene by tributylmethylammonium permanganate in dichloromethane were studied spectrophotometrically by the initial-rates method. The reaction was found to be first-order in both reactants. The activation parameters were calculated [619]. The kinetics of oxidation of uracil or thymine by Mn^{VI} in aqueous alkali to give the 5,6-dihydroxy product were studied. The reaction shows first-order dependence on [MnO_4^{2-}] and fractional-order dependence on [uracil] or [thymine] [620].

The ruthenium(V) oxo complexes LRu^{V}O and $[ORu^VCl_2(H_2O)_3]^+$ (LH_4 = EDTA, propylenediamine tetraacetic acid, *N*-hydroxy-ethyl ethylenediaminetriacetic acid) were found to be excellent catalysts in the oxygen atom transfer reactions to organic substrates. The kinetics of epoxidation of alkenes by LRu^{V}O were studied in detail [621].

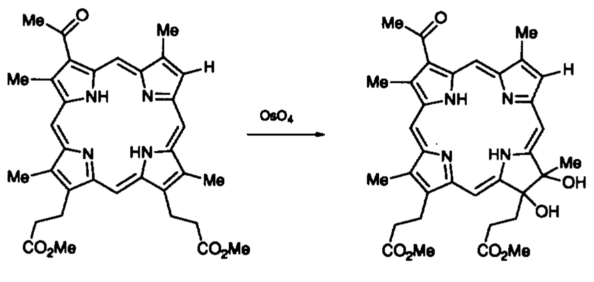
The asymmetric hydroxylations of PhCH=CHPh, $PhCH=CH_2$, and 1-phenylcyclohexene with osmium tetroxide in the presence of chiral 2,2′-bis(oxazolines) **241** were reported [622].



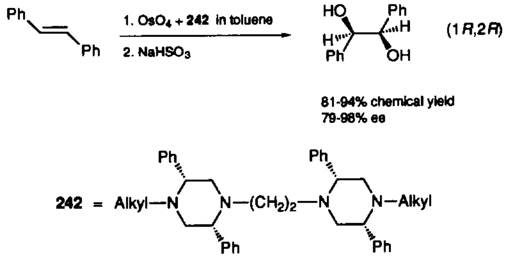
R = Me_2CH, $PhCH_2$, CH_2CHMe_2

241

Electronegative groups in porphyrins were found to direct osmium tetroxide/pyridine hydroxylations to the pyrrole subunit in the opposite quadrant of the macrocycle [623].



Effective enantioselective vicinal *cis*-dihydroxylation of olefins by a combination of osmium tetroxide and a chiral tertiary amine of bispiperazine (**242**) structure was reported [624]. *E.g.*:

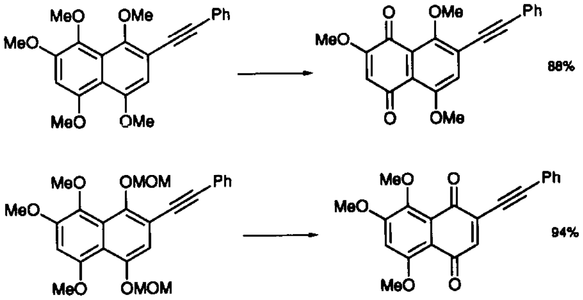


Osmium tetroxide and methylrhenium trioxide were used in dihydroxylations of various (*R*)-2-hydroxy-3-enoic acids and their derivatives. All four possible 2,3-dihydroxy-γ-butyrolactones, *i.e.*, (2*R*,3*R*,4*R*)-, (2*R*,3*R*,4*S*)-, (2*R*,3*S*,4*R*)-, and (2*R*,3*S*,4*S*)-γ-butyrolactones with different substituents in the 4-position were obtained. Depending on the derivatives and reagents applied, the diastereomeric excess achieved were 8–80% [625]. The products of asymmetric side chain dihydroxylation by osmium tetroxide of several (22*E*,24*R*)- and (22*E*,24*S*)-24-alkyl unsaturated steroids in the presence of various chiral auxiliaries were determined [626]. μ-Peroxo platinum complexes, $Pt(OOML_n)Cl(PPh_3)_2$ containing electron-withdrawing peroxo ligands $L_nM = Ph_2P(O)$, $(PhO)_2P(O)$, $PhS(O)_2$ oxidized norbornene and cyclohexene to the corresponding epoxides [627].

See also [609,611].

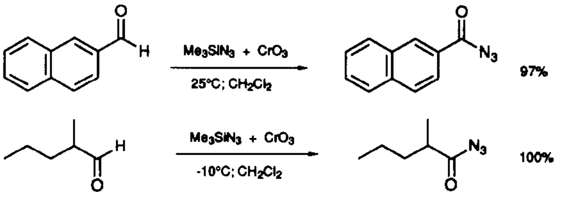
4.6.3. Oxidation of O-containing functional groups

Methoxy and methoxymethyl ethers of polyalkoxy naphthalenes were regioselectively oxidized by cerium (IV) ammonium nitrate at room temperature [628]. *E.g.*:

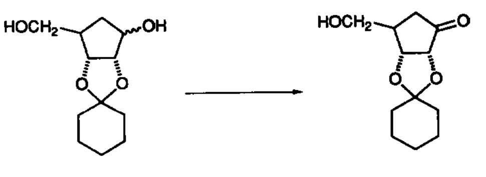


The synthesis of 2,6-di-tert-butyl-*p*-benzoquinone from 2,6-di-tert-butyl-4-methoxyphenol and 3,5-di-tert-butyl-4-hydroxybenzoic acid by Ce^{IV} and electrochemical oxidation was studied [629]. The rate of oxidation of propionic acid by cerium(IV) in aqueous perchloric acid was found to be first-order with respect to both propionic acid and cerium(IV). Linear correlation was found between log rate constant *vs.* Hammett acidity function [630]. The kinetics of oxidation of butanoic acid by cerium(IV) were studied in aqueous perchloric acid by measuring the Ce^{IV} absorbance. It was found that the reaction is first-order with respect to both oxidant and the reductant [631]. The kinetics of oxidation of formic acid by cerium(IV) in aqueous perchloric acid have been studied. The reaction shows first-order kinetics each in Ce^{IV} and formic acid [632]. The mechanism of oxidation of some naphtholsulfonic and aminonaphtholsulfonic acids with cerium(IV) in aqueous solutions of perchloric acid was studied based on kinetic results [633].

Chromium(VI) bound to anion-exchange resin has been used to oxidize alcohols to aldehydes or ketones [634]. Aromatic or aliphatic aldehydes are efficiently oxidized to acyl azides by chromic anhydride in the presence of azidotrimethylsilane at room temperature or −10°C, respectively [635]. *E.g.*:



2,3-*O*-Cyclohexylidene-D-ribonolactone (**244**) was prepared directly from 2,3-*O*-cyclohexylidene-D-ribose (**243**) by oxidation with pyridinium chlorochromate in 55–60% yield [636].

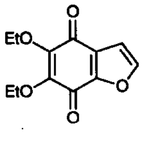


243 **244**

Cholest-4-en-3-one, stigmast-4-en-3-one, and stigmasta-4,22-dien-3-one were prepared in 73–84% yield by the reaction of pyridinium dichromate with cholesterol, β-sitosterol, and stigmasterol, respectively [637]. The synthetic potential of 1-methylimidazolium chlorochromate for the oxidation of primary and secondary alcohols has been examined. Thus, 1-octanol was oxidized to octanal in 73% yield. Borneol gave camphor in 60% yield [638]. Poly(methyl methacrylate)-based resins with bound chromium(VI) reagents selectively oxidize alcohols to the corresponding carbonyl compound. The polymer could be regenerated and re-used [639]. The kinetics and mechanism of the oxidation of benzhydrols by pyridinium bromochromate were studied [640]. The kinetics of oxidation of *para*- and *meta*-substituted benzaldehydes by pyridinium chlorochromate were studied. The reaction is first-order each in substrate, pyridinium chlorochromate and [H^+]. Electron-releasing substituents retard and the electron-withdrawing groups enhance the rate [641]. The kinetics of oxidation of D-glucose and its various C-1 and C-2 substituted derivatives by pyridinium chlorochromate were investigated. A comparison between α- and β-anomers of some monosaccharides revealed that β-anomer is oxidized faster than α-anomers [642]. The kinetics and mechanism of the oxidation of ($\pm$)-2-hydroxy-3-methyl butanoic acid by chromium(VI) in perchloric acid medium were studied [643]. A comparative study on the kinetics of oxidation of some secondary alcohols by 1-chlorobenztriazole and pyridinium dichromate between 35 and 45°C has been made. The order of reactivity diphenylcarbinol $\geq$ phenylmethylcarbinol > 2-propanol was explained in terms of an electron-releasing effect and steric strain [644]. The kinetics of chromic acid oxidation of DL-2-hydroxy-3-methylbutanoic acid in perchloric acid were studied. The reaction is first-order in Cr^{VI} and in substrate concentration. The acid concentration has a complex effect on the rate [645]. The oxidation of alcohols, aldehydes, and carboxylates by the aquachromium(VI) ion has been studied. On the basis of the kinetic and product data, the mechanism of oxidation by CrO^{2+} is proposed to be hydride transfer [646].

Oxidation of cyclohexanol, benzyl alcohol or 2-octanol by $KMnO_4$ supported on montmorillonite under sonication gave up to 100% yields of the corresponding aldehyde and ketones [647]. The kinetics of permanganate oxidation of ethylene glycol, glycol aldehyde, glycollic acid, and glyoxilic acid were studied in strong alkaline medium. A mechanism based on electron abstraction is suggested [648]. The kinetics and mechanism of the oxidation of formate and malonate with (*trans*-1,2-cyclohexanediamine-*N,N,N′,N′*-tetraacetato)satemanganate(III) have been investigated in aqueous medium. In both cases the reactions are overall second-order with first-order on both the oxidant and reductants. An inner-sphere mechanism was suggested for the formate oxidation, whereas the malonate oxidation was interpreted by an outer-sphere mechanism [649]. The kinetics of the oxidation of 2-propanol, 2-butanol, 1-butanol, and 1-pentanol to the corresponding ketone and carboxylic acid, respectively, were investigated at room temperature using cetyltrimethylammonium permanganate as the oxidant. It was shown that colloidal manganese dioxide as one of the reaction products has an autocatalytic effect [650]. The oxidation of methanol, ethanol, butanol, formaldehyde, and formic acid by permanganate in aqueous alkaline solution was studied. The deprotonation constant of these substrates was calculated from the kinetic data [651]. The kinetics of the oxidation of L-(−)-sorbose by manganese(III) in aqueous sulfuric acid was reported [652].

Quinones **245**, **236**, and **247** were prepared by oxidation of the corresponding hydroquinones by $FeCl_3$ [653].



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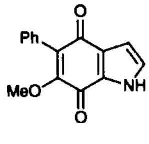

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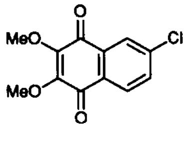
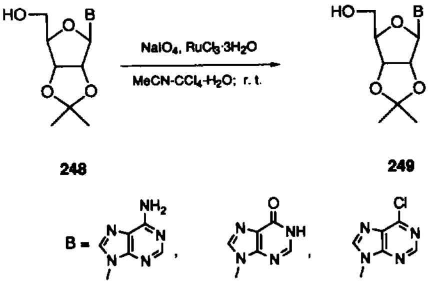


247

Inductive dihydrogen formation was observed in the oxidation of ascorbic acid by nitrosylpentacyanoferrate (II) [654]. The oxidation of L-ascorbic acid by trioxalatoferrate(III) was reinvestigated. Based on kinetic results parallel inner-sphere and outer-sphere electron-transfer reaction paths were found [655].

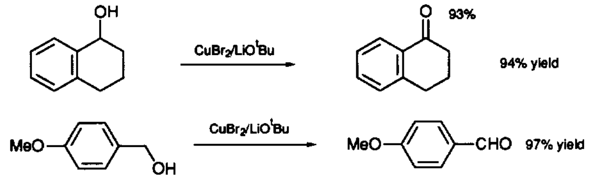
2′,3′-*O*-isopropylidene purine nucleosides **248** were oxidized with RuO_2 to provide the corresponding 5′-carboxylic acids **249** in quantitative yields under neutral conditions [656].



The oxidation of hydroquinone, 2-chlorohydroquinone, and 2,6-dichlorohydroquinone by *cis*-[$(bpy)_2(py)Ru^{IV}(O)]^{2+}$ was found to occur in distinct one-electron steps and follow pH dependent rate laws [657]. Oxo(phosphine)ruthenium(IV) complexes clearly oxidize benzyl alcohols to the corresponding benzaldehydes at 25°C. Electronic effects of *para*-substituted triphenylphosphine ligands and *para*-substituted benzyl alcohols on the rate of oxidation were investigated [658]. The kinetics of the formation of an intermediate ruthenium(III) ascorbate complex in the oxidation of L-ascorbic acid to dehydroascorbic acid by $Ru^{III}Cl_2(H_2O)_4^+$ were studied [659].

The kinetics of the oxidation of L-ascorbic acid by diaquatetraamminecobalt(III) were studied using the stopped-flow technique. The rate of oxidation is first-order with respect to both redox partners. The hydrogen ion concentration has an inhibiting effect [660].

Benzil was oxidized to benzoic acid by $(PhCO_2Cu)_4O_2(py)_2$ under argon [661]. The copper(II) reagent prepared from $CuBr_2$ and LiO^tBu was found to be a good oxidant of alcohols to the corresponding carbonyl compounds in THF at room temperature [662]. *E.g.*:



See also [589,618,687].

4.6.4. Oxidation of N-containing organic compounds

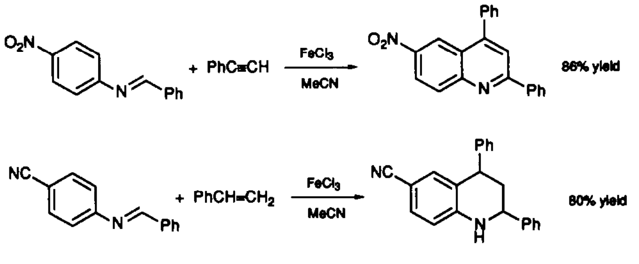
The oxidation of pyridone methyl and dimethyl derivatives with ceric perchlorate in perchloric acid medium were studied [663].

The kinetics of oxidation of alanine, valine, and phenylalanine with Cr^{VI} in prchloric acid were studied spectroscopically. The rate of oxidation is first-order in each Cr^{VI} and substrate concentrations. The order with respect to hydrogen ion concentration is complex [664].

The active oxidant of $KMnO_4 + Et_3N$ reagent was verified as MnO_4^{2-} by UV spectrometry [665]. Permanganate ion oxidized glycine in phosphate buffered solutions, and the product obtained was identified as a soluble form of colloidal manganese dioxide [666]. The kinetics of reaction between trichloroacetamide and alkaline potassium permanganate, yielding trichloroacetic acid, was investigated. The reaction is first-order with respect to concentrations of trichloroacetamide and alkali and zero-order with respect to potassium permanganate [667]. The kinetics of oxidation of glycine by permanganate ion were studied in aqueous phosphate-buffered solution at pH 6–9 [668]. A kinetic study of the potassium permanganate oxidation of L-alanine has shown that in acidic medium (pH 1–3) the autocatalytic effect is attributed to Mn^{2+} ion. The influence of factors such as amino acid and Mn^{2+} concentration, ionic strength, pH and temperature on the rate constant was analyzed [669]. The effect of reaction conditions on the kinetics of the oxidation of L-alanine by potassium permanganate in neutral aqueous phosphate buffer was studied [670]. The kinetics of permanganate oxidation of DL-alanine in aqueous perchloric acid solution were studied spectrophotometrically [671]. Addition of Mn^{2+} ion was found to accelerate the oxidation reaction. A retardation in the reaction rate was observed on addition of fluoride ion [672].

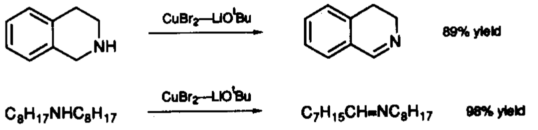
The kinetics and mechanism of the oxidation of histidine by $CoW_{12}O_{40}^{5-}$ and *trans*-cyclohexane-1,2-diamine-*N,N,N′,N′*-tetraacetatomanganate(III) was studied. Both reactions are dependent on the first powers of the concentration of the substrate and oxidant [673].

Quinolines or tetrahydroquinolines were obtained from aromatic imines and phenylacetylene or styrene, respectively, in the presence of iron(III) chloride [674]. *E.g.*:



The kinetics of oxidation of uric acid to alloxan and urea by hexacyanoferrate(III) at 45°C in acetate buffer were studied colorimetrically at 420 nm. The reaction is first-order in both oxidant and substrate [675]. The kinetics of oxidation of malonic acid dihydrazide in alkaline medium by hexacyanoferrate(III) were investigated. The results suggest that the oxidation follows a consecutive first-order irreversible path [676].

The oxidation of secondary amines with copper(II) reagent, prepared from $CuBr_2$ and LiO^tBu, at room temperature gave the corresponding imines in high yields [677]. *E.g.*:



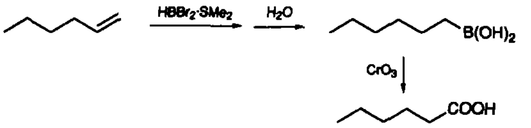
The kinetics and mechanism of oxidation of aliphatic amines by $(batho)_2Cu^{II}$ (batho = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonate) were studied. Structure *vs.* reactivity results support a mechanism involving an essentially outer-sphere initial one-electron oxidation at nitrogen, followed by loss of a proton to the solvent, where the first step is mainly rate-limiting [678].

The mechanism of the oxidative decarboxylation of amino acids by peroxydisulfate ion and catalytic silver(I) to the corresponding aldehyde at 40°C in aqueous medium was investigated [679].

4.6.5. Oxidation of Si-, P-, S-, B-, and halogen-containing organic compounds

The oxidation of glutathione by Cr^{VI} to the corresponding disulfide and the long-lived Cr^{IV} and Cr^{V} intermediates have been studied by NMR, ESR, HPLC and kinetic methods. A detailed mechanistic picture for the formation and decomposition of Cr^{IV} intermediates was presented [680]. The kinetics and mechanism of oxidation of N-substituted phenothiazines to the corresponding sulfoxides by chromium(VI) were studied. The rate of reaction in 80 : 20 = acetic acid : water is first-order each in substrate and Cr^{VI}

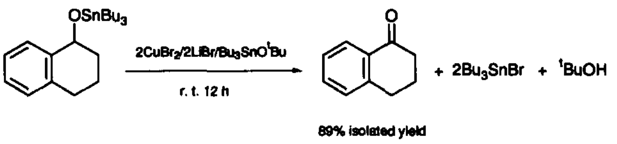
concentrations. The reaction is catalyzed by perchloric acid. Increasing the polarity of the solvent decreases the rate [681]. Alkylboronic acids, synthesized from a variety of representative terminal alkenes with dibromoborane + methyl sulfide, were oxidized with chromium trioxide in 90% aqueous acetic acid to provide carboxylic acids in 80–90% isolated yields [682]. *E.g.*:



The oxidation of BuLi, BuMgBr, BuMnCl, and $C_8H_{17}MgBr$ and several organoaluminium compounds by chromic anhydride + pyridine complex was studied. Varying the reaction conditions led to either aldehydes or carboxylic acids [683].

The mechanism of oxidation of $(4\text{-}RC_6H_4)_2SO$ (R = H, Me, AcNH, halo, NO_2) by $KMnO_4$ was investigated. Based on the observed Hammett r = 0.34 a mechanism involving nucleophilic attack by MnO_4^- on the sulfur atom of the sulfoxide was proposed [684]. The isolated and characterized reactive complex $Mn^{IV}(Cl_8TPP)(C_6F_5IOCl)Cl$ was found to give with PPh_3 in a stoichiometric reaction 1.5 equiv. of Ph_3PO, 1 equiv. of $Mn(Cl_8TPP)Cl$, and 1 equiv. of C_6F_5I. The active complex epoxidizes stilbene, oxygenates cyclohexane, and oxidizes anthracene to anthraquinone [685].

Alkoxytributylstannanes were oxidized to the corresponding carbonyl compounds in good yields under mild conditions using copper(II) bromide in the presence of lithium bromide and tert-butoxytributylstannane [686]. *E.g.*:

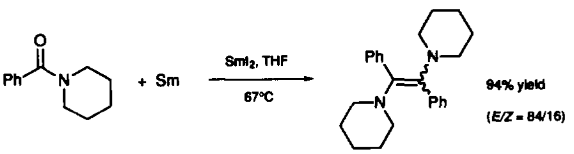


See also [618].

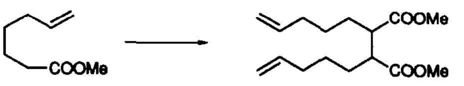
4.6.6. Oxidative coupling reactions

The oxidation of alkyl derivatives of phenol by cerium perchlorate gave quinones and/or diphenoquinones along with high-molecular-weight compounds. The effect of substituent position on the product ratio was studied [687].

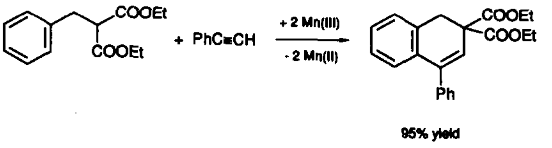
A reaction system combining SmI_2 with samarium metal accomplished the deoxygenative coupling of amides to provide *vic*-diaminoalkenes in excellent yields [688]. *E.g.*:



Oxidative dimerization of esters through their lithium ester enolates was found to be effectively promoted by $TiCl_4$ [689]. *E.g.*:

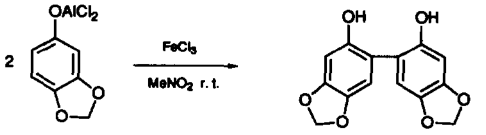


The oxidation of diethyl α-benzylmalonate by Mn^{III} acetate in acetic acid at 70°C in the presence of alkynes gave dihydronaphthalene derivatives in moderate to good yields [690]. *E.g.*:

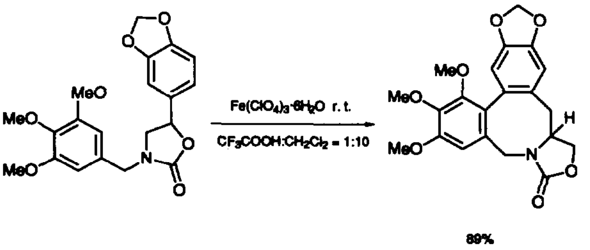


2,6-Disubstituted phenols were oxidized with Mn^{III} complexes in acetic acid. $Mn(acac)_3$ gave the corresponding 4,4′-biphenyldiols in high yields, whereas similar reactions using $Mn(OAc)_3$ gave quantitatively the corresponding 4,4′-diphenoquinones [691].

Oxidative coupling of metal phenolates by iron(III) chloride or by a mixture of iron(III) chloride and *p*-benzoquinone gave hydroxylated biaryls in up to 80% yield [692]. *E.g.*:



Iron(III) perchlorate in the presence of trifluoroacetic acid was found to be an efficient reagent for the oxidative coupling reaction of a wide variety of phenolic and nonphenolic substrates including catecholic compounds [693]. *E.g.*:

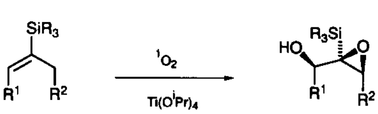


tert-Butylcyanoacetate was oxidized by hexachloroosmate(V) to decarboxylative-coupling products, *meso*- and *rac*-2,3-di-tert-butylsuccinonitrile in high yield [694].

The effect of M = Co, Ni, Cu or Zn in $py_3Cu_3M(NS)Cl_4$ (NS = monoanionic *S*-methyl isopropylidenehydrazinecarbodithioate) on the mechanisms of oxidative coupling of 2,6-dimethylphenol to the corresponding diphenoquinone was investigated [695].

4.7. Electrooxidation and photooxidation

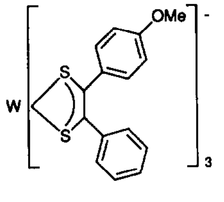
The photooxygenation of **250** in the presence of 25 mol% $Ti(O^{i}Pr)_4$ (Na lamp, tetraphenylporphine sensitize, dichloromethane, −10°C, 20 h) gave the epoxy alcohol **251** regio- and diastereoselectively [696].



250 **251**

The polyoxochromate-catalyzed photooxygenation of cyclohexane to cyclohexanol and cyclohexanone with air in dichloromethane was studied. UV observations, in conjunction with induction period studies, indicated that while $Cr_2O_7^{2-}$ is catalytically inactive, it is photochemically polymerized to catalytically active $Cr_4O_{13}^{2-}$ [697].

The catalyst regeneration by dioxygen in the photocatalytic oxidation of isopropanol by polyoxometalates of molybdenum and tungsten was studied [698]. Anionic clays pillared by $BV^{IV}W_{11}O_{40}^{7-}$, $SiV_3W_9O_{40}^{7-}$, or $H_2W_{12}O_{40}^{6-}$ ions were found to be active in the photocatalytic oxidation of isopropanol to acetone in the presence of dioxygen [699]. The complex tungsten anion **252** was found to catalyze the reaction of water with electrochemically produced methyl viologen free radical to give dihydrogen [700].

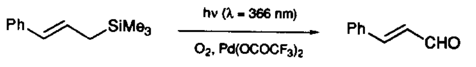


252

The photocatalytic activity of iron(III) porphyrins, "caged" into the voids of a polystyrene matrix, in the oxidation of cyclohexene to 2-cyclohexene-1-ol and 2-cyclohexene-1-one by molecular oxygen has been demonstrated [701].

The electrocatalytic oxidation of alcohols to aldehydes or ketones has been investigated by using carbon electrodes modified by functionalized polypyrrole-RuO_2 films. Best results were obtained with polypyrrole films substituted by a tris(bipyridyl)ruthenium(II) complex, the latter acting as an electron relay for the electrogeneration of the strong oxidizing species RuO_4^{2-}. Under optimum conditions a maximum turnover of 10900 was achieved [702]. The electrochemical oxidation of alcohols bearing an α-hydrogen ($^{i}PrOH$, benzyl alcohol, sec-phenethyl alcohol) have been studied in the presence of polyaminopolycarboxylate ruthenium(III) complexes. Turnover frequencies as high as 488 were reported in the case of benzyl alcohol [703]. The epoxidation of cyclohexene and cyclooctene and the oxidation of triphenylphosphine using dioxygen and $[Ru^{III}(Naphdien)Cl]$ (Naphdien = bis(2-hydroxynaphthaldehyde)diethylenetriaminato) as the electrocatalyst has been reported. Controlled potential electrolysis experiments at −0.24 V yielded primarily cyclohexene oxide, cyclooctene oxide and triphenylphosphine oxide with turnover rates of 2.3, 2.6, and 5.4 moles of product per mol catalyst per hour, respectively [704]. Photo-oxidation of cyclohexane and adamantane to cyclohexanol and 1-adamantanol, respectively, was carried out in a semiconductor particulate system containing $Pt + TiO_2 + RuO_2$ semiconductor powder, $[Ru^{III}(EDTA\text{-}H)Cl]^-$ complex as catalyst in water + dioxane [705]. The electrocatalytic DNA cleavage by oxoruthenium(IV) complexes have been studied by cyclic voltametry. A dramatic decrease in current for the $Ru^{IV/III}$ and $Ru^{III/II}$ couples upon addition of DNA to solutions of these complexes is indicative of binding of the complex to DNA [706].

Zinc, manganese, and copper ions were found to catalyze the light-dependent ascorbate oxidation [707]. The palladium(II) and (η^3-allyl)palladium complex-catalyzed oxygenation of allylsilanes under UV light gave products resulted in allylic oxidation [708]. *E.g.*:

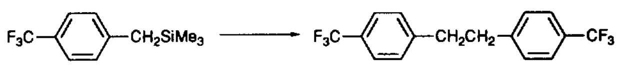


25% yield; 78% selectivity

Light-induced oxygenation of cyclohexane in acetonitrile in the presence of H_2PtCl_6 and air gave nearly equal quantities of cyclohexanol and cyclohexanone. Also the competitive oxidation of cyclohexane and ethyl benzene was studied [709]. Irradiation of cyclohexane solutions in acetonitrile in the presence of dioxygen and catalytic amounts of $FeCl_3$, $CuCl_2$, $Na[AuCl_4]$, or H_2PtCl_6 resulted in the formation of cyclohexanol and cyclohexanone with quantum yields of 0.01 to 0.05. The best results were obtained with $FeCl_3$ and l = 365 nm [710].

Cyclohexane, n-heptane, and 3-methyl-hexane were effectively oxidized to hydroperoxides by atmospheric oxygen at 15°C when their solutions in acetonitrile were irradiated by visible light in the presence of hydroquinone or quinone and catalytic amounts of $Cu(OAc)_2$. Relative reactivities of the C–H bonds of n-heptane in positions 1, 2, 3 and 4 are 1 : 15 : 15 : 5. Relative reactivities of the C–H bond at primary, secondary, and tertiary carbon atom of 3-methyl-hexane are 1 : 20 : 100 [711].

The TiO_2-mediated photochemical oxidation of substituted benzyltrimethyl-silanes in acetonitrile in the presence of Ag_2SO_4 afforded diarylethanes in 50–74% yields [712]. *E.g.*:



5. Reviews

A combined *ab initio* electronic structure and molecular mechanics study of olefin hydroformylation, polymerization, oxidation and "surface" complexation. 12 refs. [713].

Recent contributions to hydroformylation in the synthesis of pharmaceutical products. I. 47 refs. [714].

C_2 compounds from synthesis gas via organometallic catalysts. 110 refs. [715].

C_2 compounds directly from synthesis gas via organometallic catalysts. A literature highlight about the present day knowledge on organometallic homogeneous catalytic formation of C_2 compounds 118 refs. [716].

Prospects for the use of hydroformylation with cobalt catalysts. no refs. [717].

Hydroformylation catalyzed by ruthenium complexes. A review with 70 refs., including mononuclear ruthenium complexes, clusters, photochemical activation, and supported catalysts. [718].

Asymmetric hydroformylation in the synthesis of pharmaceuticals. 82 refs. [719].

Amidocarbonylation. 20 refs. [720].

NMR techniques for studies of hydroformylation. 32 refs. [721].

Achievements with BINAP-Ru^{II} complexes as catalysts for asymmetric hydrogenation of enamides, allylic and homoallylic alcohols, α,β-unsaturated carboxylic acids, and various functionalized ketones. 35 refs. [722].

Enantioselective catalysis with transition metal compounds. 27 refs. [723].

Asymmetric hydrogen transfer reactions promoted by homogeneous transition metal catalysts. 79 refs. [724].

New development in catalytic asymmetric hydrogenation. 50 refs. [725].

Some general characteristics of the action of enantioselective catalysts for hydrogenation. 29 refs. [726].

Design concepts for developing highly efficient chiral bisphosphine ligands in rhodium-catalyzed asymmetric hydrogenations. > 50 refs. [727].

Development of modified chiral dioxolane bisphosphine ligands and their use in efficient asymmetric synthesis of naturally occurring lignans using rhodium(I)-catalyzed asymmetric hydrogenation of itaconic acid derivatives as a key step. 52 refs. [728].

Chemical synthesis of optically pure compounds by asymmetric catalysis using transition metal complexes of BINAP and other chiral ligands. 42 refs. [729].

Asymmetric hydrogenation. The use of chiral catalysts for asymmetric hydrogenations to prepare enantiomerically pure compounds is reviewed. > 70 refs. [730].

Asymmetric catalysis by (*R*)- or (*S*)-BINAP-Ru^{II} complex and other chiral metal complexes. 21 refs. [731].

Asymmetric hydrogenation of olefins with chiral rhodium complexes. 3 refs. [732].

Electrochemical *versus* chemical synthesis of homogeneous catalysts for regio- and enantioselective olefin hydroformylation. 29 refs. [733].

Indirect electrosynthesis involving phase transfer catalysis. 11 refs. [734].

Electrocatalytic hydrogenation on hydrogen-active electrodes. Recent developments have shown that electrocatalytic hydrogenations can be carried out on carbon electrodes modified with metal complexes-based polymeric films. A review with 60 refs. [735].

Hydrogen transfer from transition metal hydrides: theoretical aspects. A review with 98 refs. [736].

Industrial aspects of selectivity applying homogeneous catalysis. 16 refs. [737].

Some adventures and innovations in industrial catalysis. A review with 20 refs. on heterogeneous and homogeneous catalysis. [738].

Ruthenium-catalyzed hydrogen transfer reactions and their application to oxidation of alcohols and reduction of ketones and imines. 40 refs. [739].

Copper-ligand systems for the catalytic hydride reduction of α,β-unsaturated ketones. 20 refs. [740].

Hydrogenation of carbon dioxide. 35 refs. [741].

A review of recent supported metal hydrocarbyl (alkyl, aryl, ect. functionalities) research (*e.g.*: propene hydrogenation on organoactinide surface) carried out at Northwestern University. 45 refs. [742].

Parahydrogen-induced polarization and polarization transfer in rhodium and ruthenium complex-catalyzed hydrogenation. 46 refs. [743].

Addition reactions (catalytic hydrosilylation of alkenes and 1-alkynes, silane alcoholysis, and transfer hydrogenation of alkenes) catalyzed by rhodium(II) carboxylates. 37 refs. [744].

Hydrosilylation of olefins catalyzed by transition metal complexes. 32 refs. [745].

Stereocontrol in catalyzed and uncatalyzed hydroboration. 43 refs. [746].

The selective functionalization of saturated hydrocarbons: Gif chemistry. > 34 refs. [747].

Relevance of Gif chemistry to enzyme mechanisms. A review and discussion with 37 refs. [748].

Selective functionalization of saturated hydrocarbons by Gif-type systems. 104 pp. [749].

Syntheses of epoxides at ordinary temperature and pressure by molecular oxygen using Ni^{II} complexes. 8 refs. [750].

Metal-mediated enantioselective access to unfunctionalized aliphatic oxiranes: prochiral and chiral recognition. 129 refs. [751].

Oxidation and epoxidation of organic substrates using transition metal-containing zeolite catalyst. 129 refs. [752].

Asymmetric epoxidation using Mn^{III}-salen complexes or related nickel complexes. 9 refs. [753].

Enatioselective epoxidations of simple olefins by "sodium hypochlorite/chiral Schiff base manganese complex". A review with commentary based on the research of E.N. Jacobsen *et al.* (1991). 23 refs. [754].

Modification of Sharpless reagent with metal hydride and silica gel and its application in natural product synthesis. 32 refs. [755].

Mechanism of alkene epoxidation by iron, chromium, and manganese higher valent oxo-metalloporphyrins. 49 refs. [756].

Recent advances in the asymmetric dihydroxylation of alkenes using osmium tetroxide. 101 refs. [757].

New ligands double the scope of the catalytic asymmetric dihydroxylation of olefins. no refs. [758].

Ruthenium-catalyzed oxidation of amides and lactams with peroxides was reviewed with comments based on the research of S.I. Murahashi *et al.* 4 refs. [759].

Biomimetic oxidation of amines, amides, alkenes, and hydrocarbons using transition metal-complex catalyst. 31 refs. [760].

Selective oxidations of alcohols using chromium(VI) reagents. 41 refs. [761].

Enantioselective sulfur-oxidation: synthetic applications. > 28 refs. [762].

Design of chemically robust metalloporphyrins as efficient biomimetic catalysts in oxygenation reactions. Optimum reaction conditions are pointed out in each case. A review with 97 refs. [763].

Shape-selective olefin epoxidation catalyzed by metallo "picnic-basket" porphyrins. 30 refs. [764].

Activation of carbon–hydrogen bonds in alkanes and other organic molecules using organotransition metal complexes. 24 refs. [765].

Metalloporphyrins as versatile catalysts for oxidation reactions and oxidative DNA cleavage. 577 refs. [766].

Chromium-catalyzed oxidations in organic synthesis. 301 refs. [767].

Application of lanthanide reagents in organic synthesis (oxidations and reductions among others). 241 refs. [768].

Transition metal and enzyme catalyzed reactions involving reactions with NH_3 and amines (such as addition of N–H bonds to alkenes, ammonoxidation, carbonylation reactions ect.). A review with 278 refs. [769].

The technological aspects of *p*-xylene oxidation to terephthalic acid and dimethyl therephthalate. 69 refs. [770].

Oxidation and oxygenation reactions of 3,5-di-tert-butylcatechol catalyzed by a rhodium(III) catecholate complex was reviewed based on the research of C. Bianchini, [771].

Structure–activity/selectivity correlation of oxidation catalysts. 31 refs. [772].

The oxidation of alkenes, alkynes, alkanes, alcohols, ethers, sulfides, amines and aromatic compounds was reviewed. 402 refs. [773].

Copper ion catalysis of complete and partial oxidation of propylene on X and Y zeolites: correlation of electron spin resonance and product analysis. 36 refs. [774].

Metal-catalyzed air-oxidation of cyclohexane to cyclohexanone. 16 refs. [775].

Homogeneous metal-catalyzed oxidations by molecular oxygen. 71 refs. [776].

Homogeneous catalytic oxidations using metalloporphyrin complexes with emphasis on ruthenium systems. 67 refs. [777].

Oxidation and oxygenation reactions catalyzed by ruthenium(III) complexes. 80 refs. [778].

Oxidation and reduction. A review with 423 refs. Included in the discussion were among others oxidations by metal ions, [779].

Catalytic activation of hydrogen peroxide in selective oxidation reactions. 8 refs. [780].

Liquid-phase homogeneous oxidation of aromatic hydrocarbons in polar solvents in the presence of transition metals. 49 refs. [781].

Fine chemicals by catalytic oxidation. A review with 73 refs., with emphasis on types of oxidants and catalysts, phase transfer, ligand stability, heteropolyacids and redox zeolites, and selectivity. [782].

Mercury-photosensitized C–H bond functionalization. 43 refs. [783].

Functionalization of hydrocarbons by using the Vaska-type rhodium complex ligated by trimethylphosphine under irradiation. 45 refs. [784].

6. List of abbreviations

acac	acetylacetonate
AIBN	α,α'-azoisobutyronitrile
BDPP	see **50**
BINAP	see **103**
Bn	benzyl, $PhCH_2$–
BPPM	tert-butyl 4-(diphenylphosphino)-2-(diphenylphosphinomethyl)-1-pyrrolidinecarboxylate
bpy	2,2′-bipyridine
Br_8TMP	*meso*-tetrakis(2,6-dibromomesityl)porphinato
Bz	benzoyl
CAN	ceric ammonium nitrate
CHIRAPHOS	see **102**
Cl_8TPP	*meso*-tetrakis(2,6-dichlorophenyl)porphinato
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl, η^5-C_5H_5
Cp′	methylcyclopentadienyl, η^5-C_5H_4Me
Cp*	pentamethylcyclopentadienyl, η^5-C_5Me_5
de	diastereomeric excess
DET	diethyl tartrate
DIOP	2,3-*O*-isoproylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
DIPAMP	see **54**
dippp	1,2-bis(diisopropylphosphino)propane
DMSO	dimethyl sulfoxide
DMF	*N,N*-dimethylformamide
dppb	1,4-bis(diphenylphosphino)butane
ee	enantiomeric excess
HMPA	hexamethylphosphoric triamide
NBD	norbornadiene
Men	menthyl
NMMO	*N*-methyl morpholine *N*-oxide
py	pyridine
r.t.	room temperature
salen	*N,N′*-bis(salicylidene)-ethylenediaminato
TMP	*meso*-tetramesitylporphinato
TPP	*meso*-tetraphenylporphinato
Ts	*p*-toluenesulfonyl

7. Metal index

Rh	13, 19–43, 45, 56–64, 71, 72, 77, 78, 93, 98, 107–115, 125, 132, 134– 147, 153, 159, 160, 165–167, 178, 187–190, 198, 199, 214, 216, 217, 238, 251–253, 268–281, 283–287, 313–317, 323, 356, 412, 413, 417, 513, 570
Ir	13, 91, 100, 116, 117, 148, 149, 161, 162, 206, 217, 282, 317, 396
Ni	3, 4, 89, 90, 118, 132, 203, 239–242, 258, 326, 327, 378, 414, 427, 514, 562, 571, 572, 695
Pd	65, 76, 80–83, 87–90, 92, 95, 119–125, 179, 200, 207, 240, 243–247, 257, 285, 288–292, 319, 325, 357–360, 431, 451–453, 614, 615, 708
Pt	43–46, 66, 75, 89, 90, 158, 175, 191, 257, 266, 283–287, 294–310, 324, 345, 415, 454, 616, 617, 627, 709, 710
Cu	4, 240, 241, 257, 346, 347, 357–360, 383, 384, 387–391, 397–404, 418, 419, 428, 452, 453, 514, 536, 555, 601, 661, 662, 677, 678, 686, 695, 707, 710, 711
Ag	4, 257, 563, 618, 679, 712
Au	710
Zn	249, 695, 707
Hg	257

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