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# Transition metals in organic synthesis: hydroformylation, reduction, and oxidation. Annual survey covering the year 1993 *

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## Contents

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## 1. Theoretical calculations

An ab initio MO study was carried out for hydrozirconation of ethylene and acetylene by $Cp_2^*Zr(H)Cl$. Attack of ethylene and acetylene at zirconium between the chlorine and hydrogen ligands was found to be most favorable, with a very low activation energy [1].

An ab initio MO study was carried out for two possible stereochemical reaction paths for methanol dehydrogenation to formaldehyde with $Ru(OAc)Cl(PEtPh_2)_3$, taking into account the coordination of solvent methanol to reaction intermediates [2].

A density functional study was carried out on the electronic and molecular structure of the hydroformylation catalyst $HCo(CO)_3$ as well as the parent molecule $HCo(CO)_4$. The study was based on a nonlocal density functional method. The catalyst $HCo(CO)_3$ was found to adopt a low energy singlet ground state with geometry of $C_S$ symmetry where one equatorial CO group has been removed from $HCo(CO)_4$. 169 kJ $mol^{-1}$ bond energy was calculated for the $Co–CO_{eq}$ in $HCo(CO)_4$ [3].

The solution structures of intermediates in the [rhodium(chiral bisphosphine)]$^+$-catalyzed hydrogenation of prochiral enamides were examined by molecular mechanics computation and by NOE spectroscopy. According to the calculations the principal enantiodiscriminating interaction appears to occur between the plane of the enamide ester function and the proximal arene ring of the chiral bisphosphine. The high steric energies computed by molecular mechanics cast doubt on the purported intermediacy of a six-coordinate dihydride in the catalytic asymmetric hydrogenation of prochiral enamides [4].

The effect of the migrating group R, the metal M, and the number of ancillary ligands L on the CO insertion step into the metal–carbon bond in $RML_n$ complexes was analyzed in terms of a general configuration interaction method. A numerical index was proposed for the migratory capacity of $\sigma$-bonded groups [5].

## 2. Hydroformylation and related reactions of CO

### 2.1. Hydroformylation

### 2.1.1. Cobalt catalysts

Titanium–cobalt heteronuclear clusters were synthesized by the reaction between polymer-attached titanocene and octacarbonyldicobalt. These complexes were found to catalyze the hydroformylation of ethylene [6].

The behaviour of octacarbonyldicobalt in the hydroformylation of 1-hexene in polar solvents under various carbon monoxide and dihydrogen pressures was investigated [7]. The kinetics of ethylene hydroformylation in propanal condensation products as the reaction medium were investigated [8]. The effect of water on the result of hydroformylation of 1-octene using a tributylphosphine modified cobalt carbonyl catalyst was studied. In the presence of water the rate of nonanal synthesis was found to be greater [9]. See also Refs. [11,12,14,15,42,51].

### 2.1.2. Rhodium catalysts

The time-dependent concentrations of the precursor $Rh_4(CO)_{12}$, the intermediate $C_6H_{11}CORh(CO)_4$ and the organic product $C_6H_{11}CHO$ in the homogeneous catalytic hydroformylation of cyclohexene at 10–30 °C, 10–40 bar dihydrogen partial pressure, 40–80 bar $P_{CO}$, $[Rh_4(CO)_{12}]_0 = (5\text{–}21) \cdot 10^{-6}$ mol fraction, and $[C_6H_{10}]_0 = 0.05\text{–}0.18$ mol fraction were studied in *n*-hexane solution using in situ high-pressure IR spectroscopy [10].

The hydroformylation of α- and β-pinene catalyzed by rhodium and cobalt carbonyls was investigated at 41 bar $CO:H_2 = 1:1$ [11]. The hydroformylation of 3,3-dimethylbut-1-ene was studied at 20 °C and 40 bar ($CO/H_2 = 1$) in *n*-hexane as solvent, using $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh_2(CO)_4Cl_2$, $RhCl_3 \cdot 2H_2O$, $CoRh(CO)_7$, and $Co_2Rh_2(CO)_{12}$ as catalyst precursors. The activities of all the systems can be expressed as $(d[\text{3,3-dimethylbut-1-ene}]/dt)_t = (0.138 \pm 0.028\ \text{min}^{-1})\ [{}^tBuCH_2CORh(CO)_4]_t$ [12].

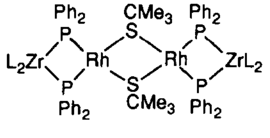
The hydroformylation of 1-hexene with **1** as the catalyst was investigated [13].

The hydroformylation of allyl alcohol and propene was studied on a $Co_2Rh_2(CO)_{12}$ based catalyst [14]. Hydroformylation and hydrocarbethoxylation of **2** and **3** have been studied in the presence of cobalt, rhodium, palladium, and platinum catalysts [15].

Activities of rhodium complex catalysts containing diphenylphosphino derivatives of polystyrene, polybutadiene, or poly(vinyl chloride) were compared in dodecene hydroformylation at 90 °C under 5 bar ($CO:H_2 = 1$). The most effective catalyst contained three phosphorus-attached aryl groups [16].

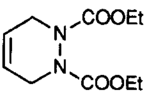
The rhodium-catalyzed 1-hexene hydroformylation was found to give improved selectivity in the presence of **4** as ligand [17].

The ammonium salt of sulfonated triphenyl phosphite, which was found to be resistant to hydrolysis, was used as a cocatalyst in the rhodium-catalyzed hydroformylation of 1-tetradecene and 1-hexene at 125 °C and 6 bar total pressure with 500 ppm and 20 ppm rhodium concentration, respectively. In comparison with tri-



L = $C_5H_4SiMe_3$

**1**



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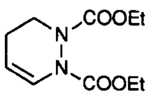

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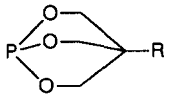


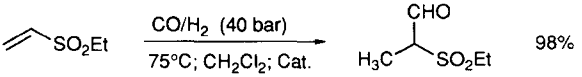
(R = Et, $C_8H_{17}$, $CH_2O_2CC_6H_{13}$, $CH_2O_2CC_6H_{13}$)

**4**

phenyl phosphite and triphenyl phosphine the sulfonated triphenyl phosphite led to higher linear/branched aldehyde ratios [18].

The hydroformylation of **5** in the presence of rhodium complexes afforded **6** and **7** as the final products [19].

The hydroformylation of vinyl sulfones and sulfoxides with exclusive formation of branched-chain aldehydes was achieved by using $\eta^6$-$C_6H_5B^-Ph_3Rh^+$(1,5-COD) and dppb (1,4-bis(diphenylphosphino)butane) as the catalyst precursors at 75 °C and 40 bar $CO/H_2 = 1/1$ in dry methylene chloride. E.g.:



Moderate diastereoselectivity and enantioselectivity was found in the hydroformylation of racemic phenyl vinyl sulfoxide using BINAP on place of dppb [20]. Cationic and zwitterionic rhodium complexes with added 1,4-bis(diphenylphosphino)butane (dppb) were found to be efficient catalysts for the highly regioselective hydroformylation of allyl acetate and related esters to yield the linear aldehyde (up to 95%) under mild conditions [21].

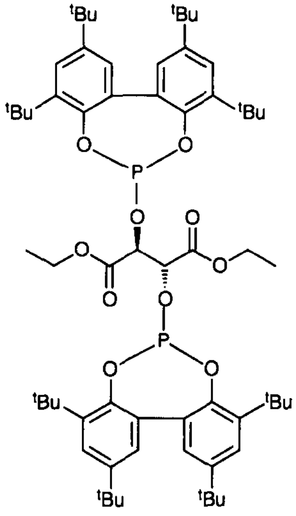
In the hydroformylation of styrene at 25–40 °C and 40 bar syngas pressure in the presence of a chiral rhodium-diphosphite catalyst (prepared in situ from $Rh(acac)(CO)_2$ and **8**) up to 35% iso/*n* ratio and 20% ee of the iso product was achieved [22].

Highly enantioselective hydroformylation of various olefins catalyzed by BINAPHOS–Rh(I) complexes (BINAPHOS = **9**) has been communicated. Thus vinyl acetate gave at 60 °C under 100 bar $CO:H_2 = 1:1$ >99% conversion to a mixture of the branched and normal aldehydes (86:14 ratio). The branched aldehyde was found to be the (*S*)-isomer in 92% ee. Similarly high enantiomeric excess was obtained in the case of *N*-vinylphthalimide (85% ee) and aryl ethenes (88–95% ee). Reaction of 1-hexene afforded the (*R*)-isomer of the corresponding branched aldehyde in 75% ee [23].

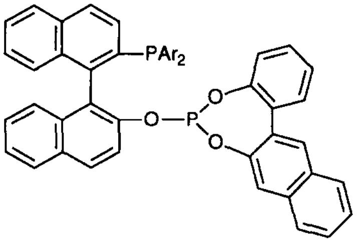
Thioalkenes, in particular 2-vinylthiophene, $PhSCH{=}CH_2$, and $2\text{-}MeSC_6H_4CH{=}CH_2$, were regioselectively hydroformylated at 35 °C and 80 bar $CO:H_2 = 1:1$ using $RhH(CO)(PPh_3)_3$ as the catalyst (iso:*n* $\leqslant 19.5:1$) with no competing hydrogenation [24].

Hydroformylation of methyl cinnamate and cinnamaldehyde diethylacetal cata-

$$\underset{\mathbf{5}}{CH_2{=}CHCH_2NEt_2} \longrightarrow \underset{\mathbf{6}}{Et_2NCH_2CH_2CH_2CH_2NEt_2} + \underset{\mathbf{7}}{Et_2NCH_2CH_2CH_2CHO}$$



**8**



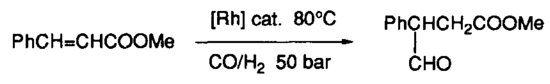
Ar = Ph, 3,5-$Me_2C_6H_3$

**9**

lyzed by various rhodium complexes affords the aldehydes **10** and **11**, respectively in good chemo- and regio-selectivity [25].

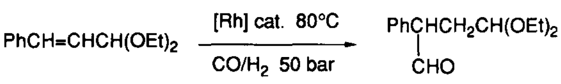
A partial study of the kinetics of the hydroformylation of alkenes catalyzed by $[Rh(SR)(CO)PR_3]_2$ and an investigation of catalyst cross-over reactions provides evidence for an active species that is mononuclear [26].

The effect of solvent on the kinetics of hydroformylation of 1-hexene using $HRh(CO)(PPh_3)_3$ as the catalyst was investigated [27]. Solvent effects of ethanol, heptanol, benzene, and toluene in hydroformylation of 1-octene using



$$PhCH{=}CHCOOMe \xrightarrow[CO/H_2\ 50\ bar]{[Rh]\ cat.\ 80^{\circ}C} Ph\underset{\displaystyle CHO}{\underset{|}{C}}HCH_2COOMe$$

**10**



$$PhCH{=}CHCH(OEt)_2 \xrightarrow[CO/H_2\ 50\ bar]{[Rh]\ cat.\ 80^{\circ}C} Ph\underset{\displaystyle CHO}{\underset{|}{C}}HCH_2CH(OEt)_2$$

**11**

$HRh(CO)(PPh_3)_3$ as the catalyst was studied. The effect of $PPh_3$ addition on the rate of the reaction and on the *n*/iso aldehyde ratio at 60 °C and $P(CO) = P(H_2) =$ 25.5 bar in those solvents were investigated in particular [28].

The hydroformylation of styrene under atmospheric pressure at 50 °C using rhodium complexes containing anionic chelating ligands as catalyst precursors combined with phosphines and phosphites gave 2-phenylpropanal with up to 95% regioselectivity [29]. The catalytic properties of the $Rh(acac)(CO)_2$-phosphorus ligand systems in the hydroformylation of ethyl acrylate were studied. In the case of aryl phosphites the catalytic systems exhibit high activities at 40 °C and 1 bar $CO:H_2 = 1:1$ to give β-formylpropionate as the main product. The catalyst with $PMe_3$ or $PPh_3$ was found to be inactive, whereas the catalyst with $P(OMe)_3$ or $P(OCH_2)_3CEt$ affords the α-formylated product [30].

The negative effect of various carboxylic acids on the yield and selectivity of 1-hexene hydroformylation catalyzed by $Rh(acac)(CO)(PPh_3)$ were studied [31].

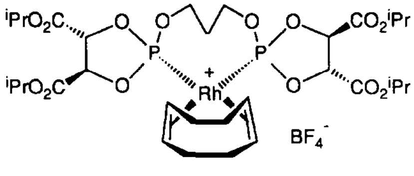
A new process of preparing 1,4-butanediol commercially was described in which allylic alcohol is hydroformylated using a rhodium catalyst in the presence of an equimolar amount of 1,4-bis(diphenylphosphino)butane to rhodium. The separation of products is carried out by water extraction [32].

The cationic rhodium complex **12** was found to be an excellent catalyst precursor for the regioselective hydroformylation of aryl olefins and methyl acrylate. At 70 °C and 100 bar $CO/H_2 = 1$, up to 97.5% branched product was obtained in the case of styrene [33].

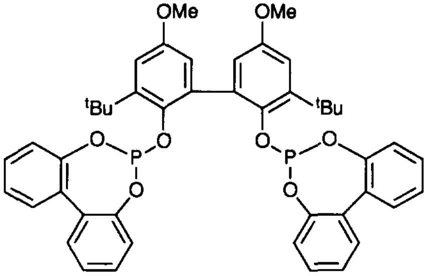
Hydroformylation of styrene at 80 °C and 40 bar $CO:H_2 = 1:1$ in the presence of a catalyst prepared in situ from $[Rh(COD)Cl]_2$ and $Ph_2PCH_2CH_2$-2-$C_5H_4N$, $Ph_2PCH_2CH_2N(CH_3)_2$, or $Ph_2PCH_2CH_2CH_2N(CH_3)_2$ gave high branched-selectivity and enhanced reaction rate compared with catalysts with $Ph_3P$, $Ph_2PCH_3$, and $Ph_2PCH_2CH_2PPh_2$ ligands [34].

The regioselective hydroformylation of a variety of functionalized α-olefins, such as $MeCO(CH_2)_2CH{=}CH_2$ and $XCO(CH_2)_nCH{=}CH_2$ (X = OMe, OH, $n = 8$; X = OBz, $NEt_2$, $n = 2$) was accomplished using an in situ generated catalyst prepared from $Rh(CO)_2(acac)$ and bisorganophosphite ligand **13** to give the corresponding aldehyde $MeCO(CH_2)_4CHO$ and $XCO(CH_2)_n(CH_2)_2CHO$, respectively [35,36].

Rhodium(I) complexes containing the atropisomeric sulfur ligands 1,1′-binaphthalene-2,2′-dithiol or the relevant dimethyl sulfide (**14**) were found to be effective catalysts for the regioselective hydroformylation of styrene. Thus, up to



**12**



**13**

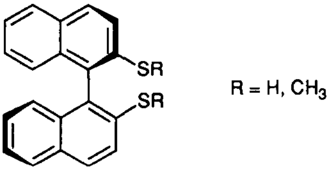
96% 2-phenylpropanal was obtained between 25 and 80 °C and 80 bar $CO:H_2=1$, but the enantiomeric excess of the (*S*)-isomer was low (2–15%) [37].

The hydroformylation of olefins using phosphine-modified rhodium catalysts has been studied under atmospheric pressure. In the case of the dodecacarbonyltetrarhodium cluster, the phosphine-modified catalyst exhibits very high activity, but a decay of catalyst activity with time was observed. In the case of $Rh(LL')(CO)_2$ complexes, containing chelate ligands with oxygen and nitrogen as coordinate atoms, the phosphine-modified catalysts were found to be fairly active and stable. All these catalysts, afford almost 100% chemoselectivity to aldehydes [38].

Vinylidene ($-CH_2-C(CH_3)=CH_2$) terminated polyisobutenes were hydroformylated with $CO/H_2$ in the presence of a rhodium catalyst to afford novel polymers carrying terminal primary aldehyde groups [39].

High regioselectivity for linear aldehydes and high reactivity was found in 1-alkene hydroformylation using bimetallic rhodium complexes with tetraphosphine ligand. A mechanism involving bimetallic cooperativity between the two rhodium centers in the form of an intramolecular hydride transfer was proposed [40]. Homobimetallic rhodium complexes with the electron-rich tetratertiary phosphine ligand $Et_2PCH_2CH_2(Ph)PCH_2P(Ph)CH_2CH_2PEt_2$ were found to be active and selective hydroformylation catalysts [41].

Hydroformylation reactions with heterodinuclear complexes, $[(CO)_4Fe(\mu\text{-}P^tBu_2)Rh(CO)L](Fe\text{–}Rh)$ ($L=CO$, $HP^tBu_2$) and $[(CO)_3Co(\mu\text{-}H)(\mu\text{-}P^tBu_2)\text{–}Rh(CO)(HP^tBu_2)](Co\text{–}Rh)$ have been reported [42]. The chloro-bridged zinc–rhodium heterobinuclear complex, $\{L[ZnCl(\mu\text{-}Cl)Rh(CO)]\}(CF_3SO_3)$ L= 2,6-bis[(3-diphenylphosphino)propoxy)methyl]pyridine, was found to be an active



**14**

hydroformylation catalyst, displaying no induction period for initiation of the reaction [43]. See also Refs. [44,45].

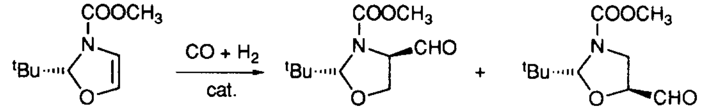
### 2.1.3. Platinum catalysts

Highly diastereoselective synthesis of **16** and **17** by catalytic hydroformylation of **15** at 100 °C and 80 bar CO : $H_2$ = 1 : 1 was reported. Using 0.5[Rh(NBD)Cl]$_2$ + dppp (dppp = 1,2-bis(diphenylphosphino)propane) as the catalyst precursor at 92% conversion a mixture of **16** and **17** in 20 and 71% yield is formed, respectively. In the case of $PtCl_2$(dppb) + $2SnCl_2$ (dppb = 1,4-bis(diphenylphosphino)butane) as the catalyst precursor **17** is formed in 76% yield at 80% conversion [44].

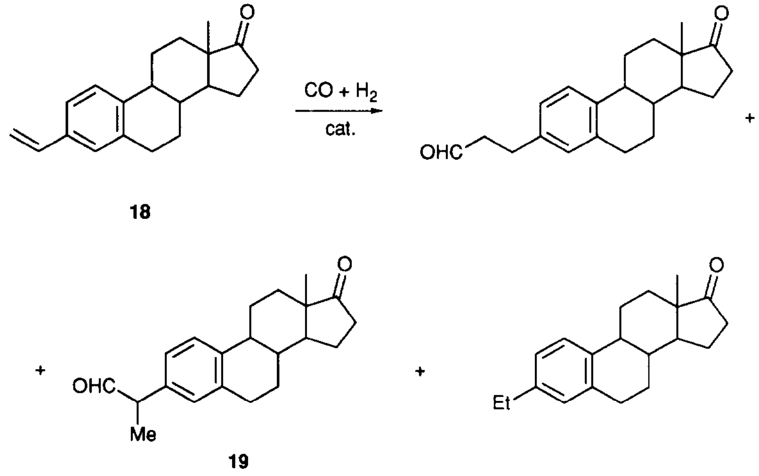
The rhodium- and platinum-catalyzed hydroformylation of **18** was found to result in a 98 : 2 ratio of epimers of **19** in up to 80% yield at 100 °C and 40 bar CO : $H_2$ = 1 : 1 in toluene [45].

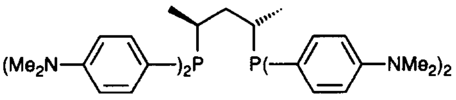
The enantioselective hydroformylation of styrene using the platinum-diphosphine-tin(II) halide catalyst was investigated. An in situ catalyst from $PtCl_2$(bdpp) (bdpp = (*S*,*S*)-2,4-bis(diphenylphosphino)pentane),2-diphenylphosphino-pyridine and tin(II) halide was found to give 86.7% ee of (*S*)-2-phenylpropanal with 31% selectivity at 40 °C and 40 bar CO : $H_2$ = 1 : 1 in toluene solvent [46]. The effect of temperature in the asymmetric hydroformylation of styrene by PtCl($SnCl_3$) complexes of **20**, **21**, and **22** has been studied [47].

The hydroformylation of norbornene catalyzed by [Pt($C_2H_4$)(dppb)]/$CH_3SO_3H$

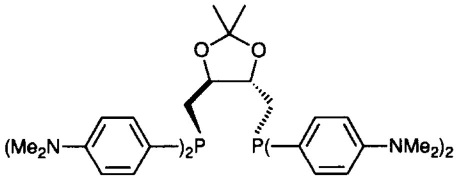


**15** **16** **17**

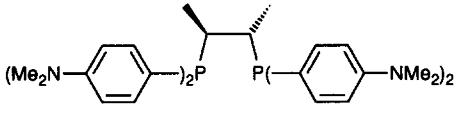




**20**



**21**



**22**

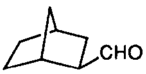
was found to give the exo-norbornanecarboxaldehyde **23** exclusively. The deuteroformylation of this olefin has shown that the addition of H and CHO groups is *cis*. The monohydroformylation of 2,5-norbornadiene using the same catalyst was also investigated [48]. See also Ref. [15].

### 2.1.4. Other metals as catalysts

Various ruthenium carbonyl complexes, such as the water-soluble and air-stable $Ru_3(CO)_9(Ph_2P\text{-}m\text{-}C_6H_4SO_3Na)_3$, were used as catalysts for hydroformylation of ethene and propene at 120 °C and 27–50 bar pressure [49].

Glycerol, erythritol, xylitol, glucose, and fructose were dehydroxylated and hydrocarbonylated to ethers, alcohols, esters, and other compounds in the presence of $Ru(CO)_4I_2$ and synthesis gas [50].

Two polymer-supported metal cluster $(POL\text{-}C_6H_4CH_2PPh_2M\text{-}\mu_3)FeCo_3(CO)_{12}$ (M = Cu, Au, POL = polystyrene-divinylbenzene) were found to be more stable and more selective as catalysts for the production of *n*-heptyl aldehyde in the hydroformylation of 1-hexene than the corresponding homogeneous clusters $(Ph_3PM\text{-}\mu_3)FeCo_3(CO)_{12}$ [51]. See also Refs. [13,42].



**23**

### 2.1.5. *Heterogeneous systems (supported complexes)*

A mixture of $Ru_3(CO)_{12}$ and 2,2′-bipyridine supported on various silicas or on glass was found to produce $C_7$-alcohols in 1-hexene hydroformylation. The best results (40–97% yield and 1.5–1.1 *n*/*i* ratio) were obtained at 150 °C and 50 bar $CO:H_2=1$ with $Ru_3(CO)_{12}$/2,2′-bipyridine bound on silica f22 (surface area 400 $m^2$ $g^{-1}$) [52].

The catalytic influence of silica-gel-, silica-alumina-gel-, and alumina-supported $Co_2(CO)_8$ and $CpCo(CO)_2$ on the conversion and selectivity in hydroformylation of 1-hexene was studied at 80 °C under 120 bar syngas pressure in acetonitrile [53]. Diphenylphosphine-containing polystyrene was used as support for tetranuclear cobalt carbonyl cluster catalyst [54].

Rhodium tetramer and rhodium-cobalt ($Rh_2Co_2$ and $RhCo_3$) carbonyl clusters attached to tris-hydroxymethylphosphine-grafted silica were found to exhibit high catalytic activity with >98% selectivity in the gas phase hydroformylation of ethene and propene to give aldehydes under mild conditions (0.04 bar and 27–100 °C) [55]. The activities of $Rh^+(CO)_2/SiO_2$, $RhCl_3/SiO_2$ and $Rh(NO_3)_3/SiO_2$ for ethene hydroformylation were studied [56]. Silica-supported rhodium tris(*m*-sulfophenyl)phosphine trisodium salt catalysts were found to show good activity and aldehyde selectivity in hydroformylation of 1-hexene and methyl 10-undecenoate when the ratio of P/Rh was 6–15 at 60–80 °C [57]. Diffuse reflectance FTIR spectroscopy was used in the characterization of silica-supported $Na_2[Rh_{12}(CO)_{30}]$ catalyst in the hydroformylation of ethene [58]. The hydroformylation of vinyl acetate was catalyzed by a silica supported aluminazane–rhodium complex to give α-acetoxypropanal in >90% yield. No β-etoxypropanal or any other product was observed. The catalyst could be reused several times without any noticeable change of catalytic activity [59].

The influence of the chain loading on the activity and complex formation of a copolymer-bound (styrene-2,2′-bis(4,6-di-t-butylphenyl)-*p*-styryl phosphite copolymer) rhodium hydroformylation catalyst in comparison with its low molecular weight analogue were studied. It was found that low chain loadings give an active catalyst [60]. The hydroformylation of styrene at 100 °C and 30 bar $CO:H_2=1:1$ in a continuous flow reactor was studied using silica-grafted polymer-bound phosphite modified rhodium complexes as the catalyst. In benzene as the solvent constant conversions over a period of at least ten days were observed [61].

The gas phase hydroformylation of propene at 133 °C and 11 bar (propene:$CO:H_2=2.4:2$, 2:1.0) was catalyzed by a cationic rhodium carbonyl complex co-ordinatively bound to a copolymer of 2-vinylpyridine and methyl acrylate crosslinked with 5 mol% ethene diacrylate. The observed ratio of *n*-butyraldehyde/isobutyraldehyde was close to 1 [62]. Poly(trimethylpropane)-trimethacrylate-bound rhodium phosphine complexes were studied in continuous gas-phase hydroformylation of propene. At 60 °C and $P_{tot}=0.6$ bar, these catalysts were found to be highly active with total hydroformylation rates between 3 and $110 \cdot 10^{-6}$ mol butanol $s^{-1}$ (g $Rh^{-1}$) and also highly stable showing no loss in activity after 215 h on stream [63]. A polymer bound rhodium–phosphine complex was tested in continuous liquid-phase hydroformylation of 1-hexene at 25 bar total pressure and 60–100 °C. At 100 °C the heptanal/methylhexanal ratio was found to be 3.7 [64].

Rhodium complexes with water-soluble sulfonated polyphenylene sulfide were used as catalysts in hydroformylation of methyl ω-undecylenoate in a two-phase system [65].

Palladium trimethylphosphine carbonyl clusters in zeolite NaY were studied as catalysts for propene hydroformylation at medium pressure [66]. New silica-supported catalysts from *cis*-$[PtCl_2(PPh_3)_2]$ and $SnCl_2$ were found to be active in the hydroformylation of ethylene [67]. Catalyst prepared from *cis*-$[PtCl_2(PPh_3)_2]$ and $SnCl_2 \cdot 2H_2O$ anchored on silica carrier was found to be active and selective for hydroformylation of 1-pentene. Selectivity to *n*-hexanal was as high as 94.4% at 39.2% conversion [68]. See also Ref. [51].

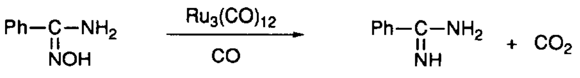
## 2.2. Hydrogenation (reduction) of CO to oxygen-containing organic compounds

A three component catalytic system consisting of (i) elemental sulfur or sulfur compounds ($CS_2$, $H_2S$, COS), (ii) an alkali methoxide or triethylamine, and (iii) vanadium compounds ($V_2O_5$, $NH_4VO_3$) was used as the catalyst for the reductive carbonylation of nitrobenzene to methyl *N*-phenylcarbamate with carbon monoxide and methanol at 150 ± 2 °C and an initial carbon monoxide pressure of 100–140 bar at 25 °C [69].

The catalytic activity of a series of ruthenium(III)-Schiff base complexes (**24**–**27**) was reported for the reductive carbonylation of nitrobenzene to phenylurethane in ethanol at 160 °C and 15 bar CO partial pressure [70].

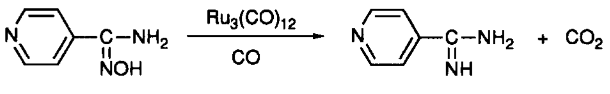
Pentacarbonyliron/sulfur was found to be an excellent catalyst precursor for liquefaction of Yallourn coal using alcohol and carbon monoxide as the reagents. The reaction at 375 °C for 120 min, or in two-staged heating (60 min at 375 °C and than 60 min at 425 °C) at 70 bar CO pressure gave high conversion and high oil yield [71].

High catalytic activity of $Ru_3(CO)_{12}$ was found for the selective deoxygenation of aromatic and *N*-heteroaromatic amidoximes to the corresponding amidines at 80 °C and 5 bar CO pressure [72]. E.g.:

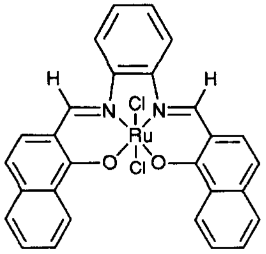


$$Ph{-}\underset{\underset{NOH}{\|}}{C}{-}NH_2 \xrightarrow[CO]{Ru_3(CO)_{12}} Ph{-}\underset{\underset{NH}{\|}}{C}{-}NH_2 + CO_2$$

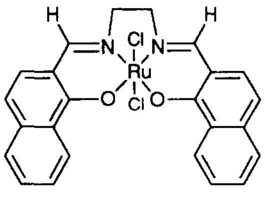
82% yield



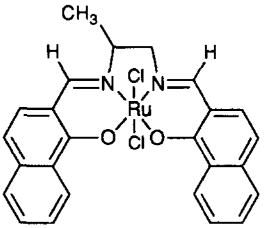
45% yield



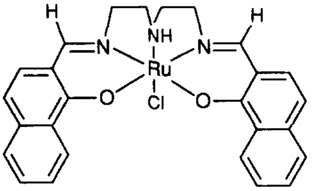
**24**



**25**

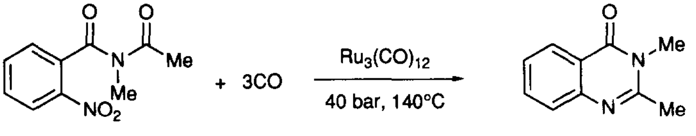


**26**



**27**

4(3*H*)-Quinazolinone derivatives were prepared in high yields by the $Ru_3(CO)_{12}$-catalyzed reductive *N*-heterocyclization of the corresponding *N*-(2-nitrobenzoyl)-amides under carbon monoxide pressure [73]. E.g.:



93% isolated yield

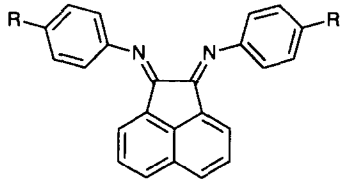
The effects of various ligands on the catalytic properties of palladium complexes in the synthesis of *N*,*N*′-diphenylurea from nitrobenzene, anilin and carbon monoxide was studied. Compared to monodentate phosphines, bidentate ligands showed higher activity [74].

### 2.3. *Water gas shift reaction and reduction with* $CO$, $CO + H_2$, *or* $CO + H_2O$

The reduction of nitrobenzene to aniline by $CO/H_2O$ in the presence of $Ru_3(CO)_{12}$ and the rigid α-diimine ligand **28** was reported [75].

Cellulose acetate films impregnated with $RuCl_3 \cdot H_2O$ were found to show catalytic activities in oxidation of carbon monoxide to carbon dioxide and the water–gas shift reaction under relatively mild conditions (< 150 °C) [76].

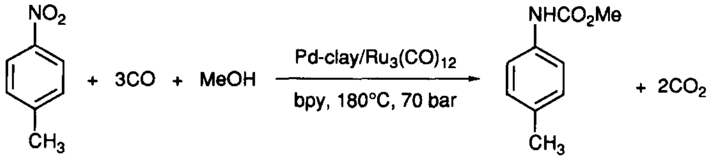
High catalytic activities for the selective reduction of aromatic nitro compounds



R = $CH_3$, Cl, $OCH_3$

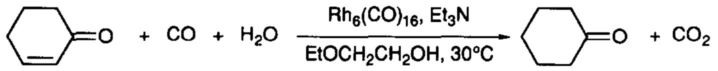
**28**

to aromatic amines were found by chelatephosphine added rhodium and ruthenium complexes at room temperature and atmospheric pressure of carbon monoxide in a sodium hydroxide aqueous solution [77]. Reductive carbonylation of various mono- and dinitroarenes at 180 °C and 70 bar CO pressure in alcohol solution catalyzed by montmorillonitebipyridinylpalladium(II) acetate and $Ru_3(CO)_{12}$ afforded the corresponding urethane selectively [78]. E.g.:



97%

The carbon–carbon double bond of various $\alpha,\beta$-unsaturated carbonyl compounds was selectively hydrogenated at room temperature under atmospheric pressure of carbon monoxide using a $Rh_6(CO)_{16}$–$Et_3N$ catalyst system [79]. E.g.:



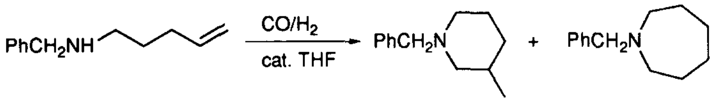
100% conversion

100% selectivity

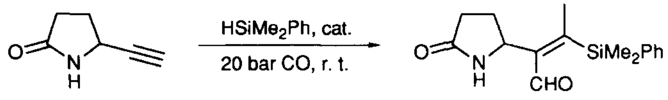
### 2.4. Hydroformylation-related reactions of CO

The reaction of Li[$HFe(CO)_4$] with styrene under 1 bar carbon monoxide in a $H_2O/^{i}PrOH/LiOH$ system was found to afford 2-phenylpropionic acid in 98% yield. In contrast, when conducted under argon, the reaction predominantly (90%) leads to 3-phenylpropionic acid [80].

The catalytic system: $Ru_3(CO)_{12}$, $Bu_4PBr$, $Bu_3P$, HCl was found to convert the alkyl part of alkyl formates into the next higher alcohol without initial gas pressure at 200–220 °C with up to 80% selectivity. Yields and turnovers decrease sharply with increasing size of the alkyl group [81].



**29** **30** **31**

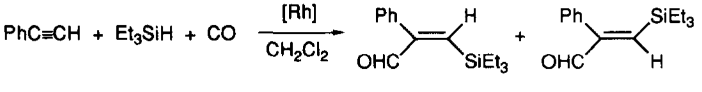


**32** **33**

The selective preparation of aliphatic primary amines from an olefin, $CO + H_2$, and ammonia was developed using octacarbonyldicobalt, phosphine ligand, and an ether or acetamide solvent system at 200 °C and 140 bar. In the case of 1-hexene this so called oxoamination yields a mix of $C_7$ and $C_{14}$ primary amine with 32 and 25% selectivity, respectively [82]. The one-pot aminomethylation of 1-octene with diethylamine at 18 bar $CO:H_2 = 1:1$ and 80 °C in the presence of $[Rh_2(\mu\text{-}S^tBu)_2(PPh_3)_2]$ as the catalyst resulted in 99% conversion of the olefin and 80% yield of diethylnonylamine [83]. The $HRh(CO)(PPh_3)_3$-catalyzed hydrocarbonylation of **29** at 100 °C and 124 bar $CO:H_2 = 1:1$ was found to give almost exclusively **30** in 85% yield. The addition of 5 equiv. of tricyclohexylphosphine or 20 equiv. of triphenylphosphine to $HRh(CO)(PPh_3)_3$ reverses the regioselectivity completely in favor of the formation of **31** [84].

The mechanism of the rhodium- and iodide-catalyzed carbonylation of methanol to acetic acid has been studied by spectroscopic methods. The key intermediate, $[MeRh(CO)_2I_3]^-$ was detected and characterized using FTIR and low-temperature $^{13}C$ NMR spectroscopy, coupled with $^{13}C$ isotopic labeling [85].

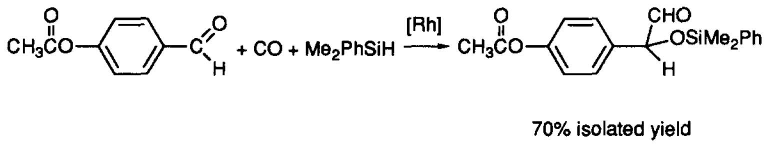
Rhodium(II) perfluorobutyrate was found to be an effective catalyst for silylcarbonylation of terminal acetylenes in reactions performed at atmospheric pressure and at or below room temperature. (*Z*)-β-Silylacrylaldehydes were formed in good to high yields [86]. E.g.:



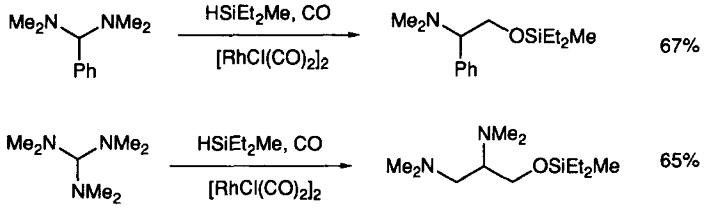
82% yield (*Z*:*E* = 10:1)

Silylformylation of **32** with $HSiMe_2Ph/CO$ at room temperature in the presence of 0.8 mol% $Rh(acac)(CO)_2$ gave **33** in 97% yield [87].

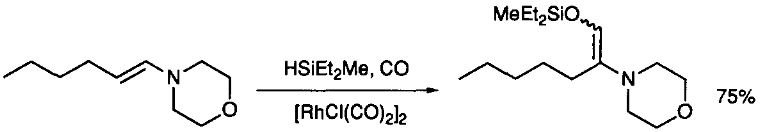
Various aldehydes were silylformylated to the corresponding α-silyloxyaldehydes in 50–90% yields using dimethylphenylsilane and $[(COD)RhCl]_2$ as the catalyst precursor at 23 °C and 17 bar CO pressure [88]. E.g.:



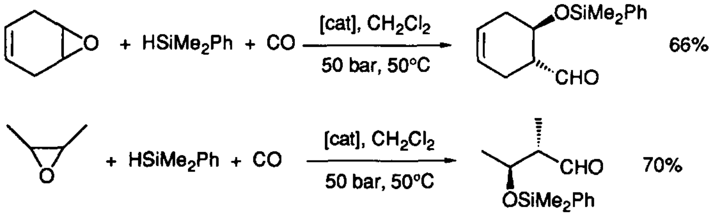
The reaction of *N*,*N*-acetals with hydrosilane and carbon monoxide at 140 °C and 50 bar CO in the presence of $[RhCl(CO)_2]_2$ as the catalyst was found to result in incorporation of CO with cleavage of one of the carbon–nitrogen bonds in the substrate [89]. E.g.:



Under the same experimental conditions enamines gave α-(siloxymethylene) amines [90]. E.g.:



The reaction of epoxides with hydrosilane and carbon monoxide in the presence of $[RhCl(CO)_2]_2$ and 1-methylpyrazole was found to result in ring-opening silylformylation leading to β-siloxy aldehydes [91]. E.g.:



The reductive carbonylation of methanol to acetaldehyde was found to be effectively catalyzed at 140 °C and 70 bar using $Rh(CO)_2(acac)/Ph_2PCH_2CH_2CH_2PPh_2$ as the catalyst precursors. Crystalline acetyl complexes $Rh(diphosphine)(COMe)I_2$ were isolated quantitatively after catalysis. Addition of ruthenium to the catalyst results in the in situ hydrogenation of acetaldehyde to ethanol [92].

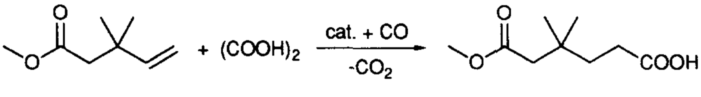
The $PdCl_2(PPh_3)_2/Ru_3(CO)_{12}$ bimetallic system was found to exhibit higher catalytic activity for the formylation of aryl and alkenyl iodides than $PdCl_2(PPh_3)_2$ or $Ru_3(CO)_{12}$ alone at 70 °C under 100 bar $CO:H_2=1:1$. The improved catalytic activity of the Pd–Ru system was attributed to the high hydrogenolysis activity of in situ generated ruthenium hydride species [93].

The hydrocarboxylation of olefins with oxalic acid at 150 °C and 20 bar CO pressure was catalyzed by palladium acetate, with added 1,4-bis(diphenylphosphino)butane and triphenylphosphine in 1,2-dimethoxyethane [94]. E.g.:

$$PhCH{=}CH_2 + (COOH)_2 \xrightarrow[-CO_2]{cat. + CO} PhCH_2CH_2COOH + PhCH(CH_3)COOH$$

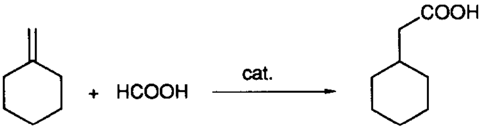
85 : 15

86% yield



90% yield

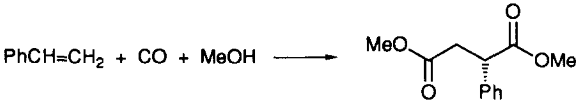
Hydrocarboxylation of methylenecycloalkanes in the presence of formic acid and carbon monoxide was found to give selectively the corresponding cycloalkylacetic acids at 150 °C and 6.8 bar CO in the presence of catalytic amount of palladium acetate and 1,4-bis(diphenylphosphino)butane in 1,2-dimethoxyethane [95]. E.g.:



94%

Alkynes were hydrocarboxylated with formic acid in the presence of catalytic amounts of $Pd(OAc)_2$ and $PPh_3$ or $Ph_2P(CH_2)_4PPh_2$ at 110–110 °C and 80 bar CO pressure to produce the corresponding unsaturated carboxylic acids in 60–90% yields [96].

Enantioselective bis-methoxycarbonylation of styrene was achieved using an in situ catalyst $Pd(acac)_2$/**34**/4-$MeC_6H_4SO_3H$ at 350 bar CO and 50 °C in the presence of *p*-benzoquinone as oxidant [97].

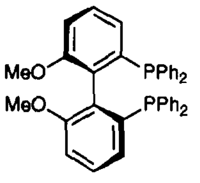


40% yield, 93% ee

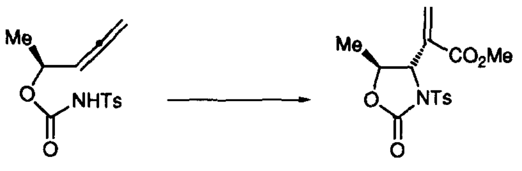
The hydrocarboxylation of α-olefins using palladium dichloride complexes with phosphoryl- and thiophosphoryl-substituted phosphines was studied. In the case of $Ph_2P(CH_2)_2P(=O)Ph_2$ >80% regioselectivity was achieved calculated with respect to the products of normal structure. The effect of the ligand used and triphenylphosphine on the catalytic system were compared [98].

Aminocarbonylation of **35** and **37** in methanol solution under CO (1 bar) at 30 °C in the presence of $PdCl_2$ (0.02 eq), $CuCl_2$ (2.0 eq) and a base (3 eq) provided stereoselectively **36** and **38**, respectively, in high yields [99].

The complex $[PdCl_2(PPh_3)_2]$ was found to be a good catalyst precursor for the

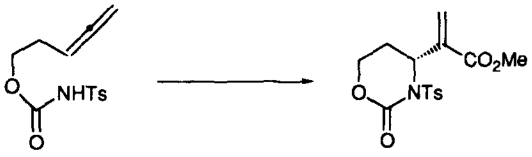


**34**



88% isolated yield

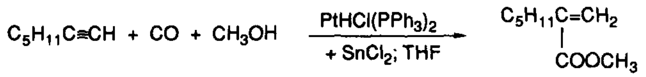
**35** **36**



90% isolated yield

**37** **38**

alkoxycarbonylation of various naturally occurring allylbenzenes, propenylbenzenes and monoterpenes at 40 bar CO pressure and 100 °C. The addition of $SnCl_2 \cdot 2H_2O$ to the catalytic system increases the selectivity to linear ester [100]. Phenylacetylene and 1-heptyne were hydrocarbomethoxylated at 100 °C and 100 bar CO pressure in the presence of Pt(II)/$SnCl_2$ system to give the corresponding $\alpha,\beta$-unsaturated esters. The complex $PtHCl(PPh_3)_2$ gave carbonylation exclusively at the $\beta$-position, whereas using $PtCl_2$(dppb) the substrates are almost exclusively carbonylated at the $\alpha$-position [101]. E.g.:



$$C_5H_{11}C\equiv CH + CO + CH_3OH \xrightarrow[+\,SnCl_2;\ THF]{PtHCl(PPh_3)_2} \underset{\displaystyle COOCH_3}{C_5H_{11}C{=}CH_2}$$

70%

$$C_5H_{11}C\equiv CH + CO + CH_3OH \xrightarrow[+\,SnCl_2;\ toluene]{PtCl_2(dppb)} C_5H_{11}CH{=}CHCOOCH_3$$

50%

*S*-Alkyl alkanethiosulfonates and sulfonic acids in a 1 : 1 ratio were obtained from aliphatic alkenes, such as propene, $SO_2$ (8 bar) and $H_2$ (25 bar) at 80 °C in the presence of $[Pd(Ph_2P(CH_2)_nPPh_2)(MeCN)_2][BF_4]_2$ ($n = 2, 3, 4, 5$) as the catalyst [102]. See also Ref. [122].

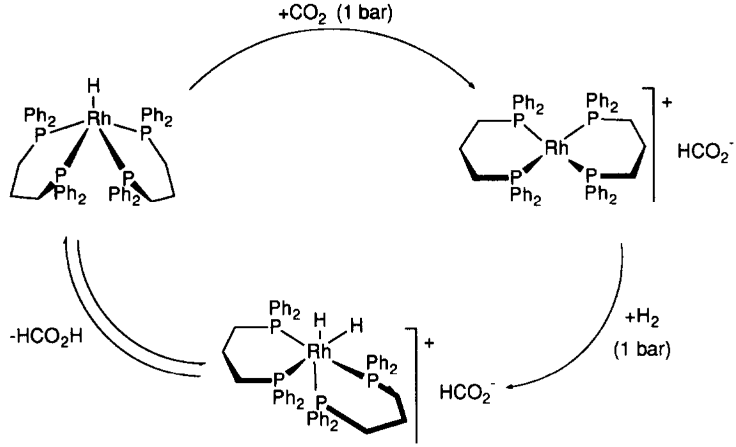
$$RCH{=}CH_2 + SO_2 + H_2 \xrightarrow{cat} RC_2H_4SO_2H \longrightarrow RC_2H_4SO_2SC_2H_4R + RC_2H_4SO_3H + H_2O$$

## 2.5. Reduction of $CO_2$

The hydrogenation of $CO_2$ in the presence of $Ru_3(CO)_{12}$ and potassium iodide at 240 °C and 140 bar was found to result in the successive formation of carbon monoxide, methanol and methane [103].

The electroreduction of carbon dioxide catalyzed by cobalt tetraphenylporphine in DMF solution was investigated by means of cyclic voltametry. The rate constant for the electron transfer from CoTPP dianion to $CO_2$ was determined. The activation energy of this reaction was estimated as 34.5 kJ $mol^{-1}$ [104].

Intermediates of the catalytic cycle of the rhodium-catalyzed hydrogenation of carbon dioxide to formic acid were detected by $^1H$ NMR spectroscopy at 22 °C and 1 bar [105].



Water-soluble sulfonated phosphane-rhodium complexes in a biphasic water-triethylamine mixture or in a homogeneous water-dimethylamine solution were found to be very efficient catalysts for the hydrogenation of carbon dioxide to formic acid at room temperature and 40 bar $CO_2 : H_2 = 1 : 1$. Under these conditions using $0.54 \cdot 10^{-3}$ M rhodium concentration 3439 turnovers give a 1.76 M solution of formic acid in 12 h [106].

Transition metal-catalyzed reaction of $Na_2CO_3$ with water at 150 °C afforded oxygen-containing compounds (carbonyl compounds and esters), aromatic compounds and paraffinic hydrocarbons. The yield of organic compounds was 10–15% based on carbonate and their calorific value ranged from 4460 to 10570 cal $g^{-1}$ [107].

## 3. Hydrogenation and reduction

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

A fast H/D exchange was found between deuterated aromatic solvents and hydride ligands of $(Cp_2^*YH)_2$. For toluene, a preference for H/D exchange on the *para* and *meta* position was found [108].

The manganese *p*-methylbenzoyl complex $Mn(CO)_5C(=O)$-4-Me-$C_6H_4$ was found to catalyze the SiH/SiD exchange between $DSiMe_2Ph$ and $HSiMe_2Et$ at room temperature in $C_6D_6$. Based on kinetic results coordinatively unsaturated manganese silyls $(CO)_4MnSiMe_2R$ were suggested as the active catalysts [109].

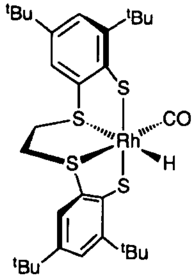
The tetradentate thioether thiol complex **39** was found to catalyze the deuteration of EtOH by $D_2$ to give EtOD [110]. See also Refs. [155,203].

### 3.2. *Hydrogenation of olefins*

### 3.2.1. *Fe, Ru, and Os catalysts*

The hydrogenation of coal tar pitch in the presence of $Mo(CO)_6$, $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$ and $Ru(acac)_3$ as the catalysts was investigated using a tritium tracer method $Ru_3(CO)_{12}$ was found to be the most active for the hydrogen transfer (hydrogen addition and exchange reactions) from the gas phase to the pitch among the metal complexes [111].

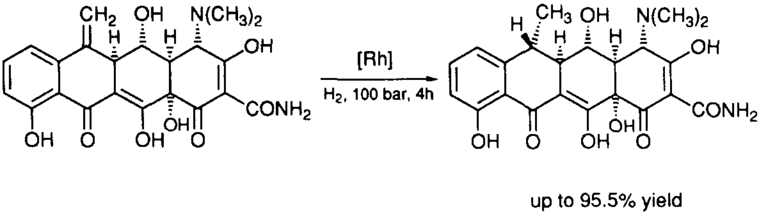
$\mu$-Phosphido stabilized di- and triruthenium clusters on a silica support were found to be active catalysts for 1-octene hydrogenation at 140 °C and 54 bar dihydrogen pressure [112]. The kinetics of cyclohexene hydrogenation using polymer-supported ruthenium(III) complexes as the catalysts were studied [113]. In the hydrogenation of 1-octene at 1 bar pressure and 70 °C using a $Ru_3(CO)_{12}$/15MeCN catalytic system, turnover numbers up to 1000 were observed [114]. The selective hydrogenation of the carbon–carbon double bonds in nitrile rubber under 50 bar dihydrogen pressure was found to be effectively catalyzed by $RuCl_2(PPh_3)_3$–$NH_4PF_6$–$Et_3N$ catalyst [115]. See also Ref. [203].



**39**

### 3.2.2. Co, Rh, and Ir catalysts

The hydrogenation of methacycline hydrochloride to α-doxycycline in methanol was studied by using novel rhodium–carborane complexes as the catalysts [116].



Dihydro(1,3-diphenyltriazenido)bis(triphenylphosphine)rhodium(III) was found to be an effective catalyst for the homogeneous hydrogenation of cinnamic acid at 30 °C and 1 bar $H_2$ [117]. The effect of phosphonium salt formation on the kinetics of homogeneous hydrogenations in water utilizing a rhodium *meta*-sulfonatophenyl-diphenylphosphine complex was studied [118]. The effect of water on the mechanism of hydrogenations catalyzed by rhodium phosphine complexes was studied [119].

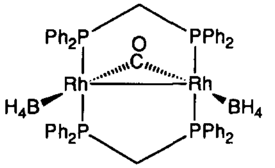
Cationic rhodium complexes with different diastereomers of phosphirane were found to show different catalytic behavior in olefin hydrogenation [120]. Cationic rhodium(I) complexes with bis(2-diphenylphosphinoethyl)amide derivative of commercial block copolymers of ethylene oxide, propylene oxide, and ethylene oxide were found to have inverse temperature-dependent solubility in water. Homogeneous catalytic hydrogenation of allyl alcohol or α-acetamidoacrylic acid using these complexes readily occurs at 0 °C but stops around 50 °C owing to the phase separation of the catalyst [121].

The catalytic performance of homogeneous and silica-anchored rhodium carbonyl complexes was studied in hydrogenation, hydrosilylation and methanol carbonylation. In hydrogenation and hydrosilylation of 1-octene, the heterogenized catalysts were found to be more active than their homogeneous analogs [122].

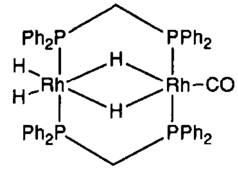
The binuclear rhodium hydride complexes **40**, **41**, **42**, and **43** were found to catalyze ethylene hydrogenation under ambient conditions [123].

The effects of catalyst site accessibility on the activities of supported olefin hydrogenation catalysts prepared from $[Rh(NBD)L_2][NO_3]_3$ ($L=Ph_2P(CH_2)_nPMe_3^+$; $n=2$, 3, 6, or 10) and a cation-exchange resin were examined. The most active catalysts are those containing the longer-chain ligands, where the catalyst sites are the farthest removed from steric hinderance by the resin surface [124]. The scope and mechanism of alkene hydrogenation/izomerization catalyzed by complexes of the type $R_2E(CH_2)_2M(CO)(L)$ (R = Cp, Me, Ph; E = P, Ta; M = Rh, Ir; L = CO, $PPh_3$) has been studied [125].

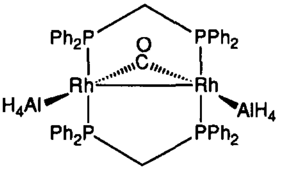
Intercalation of the olefin hydrogenation catalysts $[Ir(COD)(PPh_3)_2]^+$ and $[Ir(COD)(NCMe)(P^cHex_3)]^+$ into montmorillonite clay via an ion-exchange procedure was found to result in a lower initial activity but in a longer lifetime [126]. The complex $[(triphos)Ir(H_2)(C_2H_4)]BPh_4$ (triphos = $MeC(CH_2PPh_2)_3$) was found to be an effective catalyst for the hydrogenation of ethylene in the solid state at



**40**



**41**



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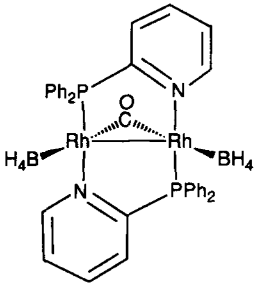


**43**

60 °C. Comparisons were made with analogous fluid solution-phase systems [127]. See also Ref. [195].

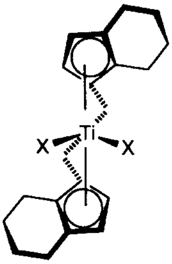
### 3.2.3. Ni, Pd, and Pt catalysts

Unsaturated triglycerides of vegetable oils were hydrogenated in the presence of nickel stearate and triethylaluminium as the catalyst under mild conditions. Poisoning of the catalyst does not occur during hydrogenation of sulfur-containing rapeseed oil [128]. The kinetics of hydrogenation of methyl (*Z*)- and (*E*)-9-octadecenoate catalyzed by a nickel(II) 2,4-pentanedionate/triethyl aluminium system were studied by initial rate measurements. In both cases the hydrogenation was found to be first-order in dihydrogen, zero-order in the octadecenoate and a fractional-order (close to one) in the catalyst [129].

Ni(saloph) (saloph = bis(salicylaldehyde)-*o*-phenylenediamine) was found to catalyze the hydrogenation of cyclohexene and cyclooctene at 50 °C and 60 bar dihydrogen pressure and the epoxidation of these olefins in the presence of $KHSO_5$ [130].

An effective Ziegler–Natta catalyst for hydrogenation of vegetable oils were prepared from nickel stearate or nickel 2-ethylhexanoate with sodium bis(2-methoxyethoxy)dihydroaluminate in toluene or *n*-heptane. The catalyst could be removed from the hydrogenated product by washing with phosphoric acid or by alkaline refining [131].

Polymer-bound palladium tetrakis(*p*-hydroxyphenyl)porphyrin complex was studied as a hydrogenation catalyst for methyl acrylate [132]. The catalytic activity of palladium(II) acetate coordinated to cross-linked polymeric isocyanides was



$X_2$ = 1,1'-binaphth-2,2'-diolate

**44**

studied. These macromolecular complexes were found to be the precursors of the hydrogenation of 1-hexene, 1,5-cyclooctadiene, phenylacetylene, benzaldehyde, *trans*-2-hexenal, and nitrobenzene at room temperature under 2 or 3 bar dihydrogen pressure [133].

The selective hydrogenation of the carbon–carbon double bond of $\alpha,\beta$-unsaturated ketones and aldehydes was achieved at room temperature and atmospheric pressure with $[(^tBu_2PH)PdP(^tBu)_2]$ after activation the catalyst with oxygen [134]. See also Refs. [171,207].

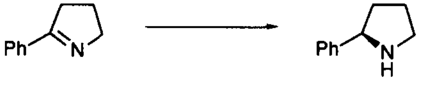
### 3.2.4. Other metals as catalysts

The catalytic hydrogenation of 1-hexene, 4-methyl-2-pentene, cyclohexene, styrene, isoprene, 1,3-cyclooctadiene, and 1,5-cyclooctadiene was studied by using different dicyclopentadienyl-titanium and -zirconium complexes as the catalysts at 90 °C and 7 bar dihydrogen pressure [135]. Silica grafted hafnium hydride complexes were found to catalyze the hydrogenolysis of neopentane and butane, and the hydrogenation of isobutene and propene under mild conditions [136]. See also Refs. [111,183].

## 3.3. Asymmetric hydrogenation of prochiral compounds

### 3.3.1. Asymmetric hydrogenation of olefins

Highly enantioselective catalytic hydrogenation of unfunctionalized trisubstituted olefins were achieved using **44** as the catalyst precursor. Addition of 1.95 equiv of *n*-butyllithium under dihydrogen at 0 °C generates the active catalyst, which is stabilized by the addition of 2.5 equiv of phenylsilane. Hydrogenations at 65 °C and 138 bar dihydrogen afforded 70–94% yield and 83–99% ee [137]. The same catalyst affords amines with excellent enantioselectivity, 95–99% ee and 71–86% yield in the asymmetric hydrogenation of cyclic ketimines either at 65 °C and 5 bar or at 21–45 °C and 33 bar dihydrogen pressure [138]. E.g.:



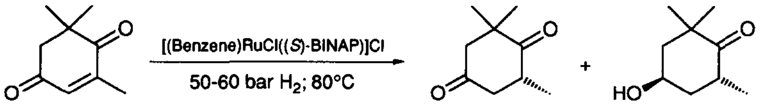
99% ee; 86% yield

Enantioselective hydrogenation of 4-oxoisophorone (**45**), catalyzed by BINAP–Ru(II) complexes gave the corresponding saturated diketone **46** in 80% chemical yield and 50% ee. The monoalcohol **47** was formed as a byproduct of the hydrogenation [139].

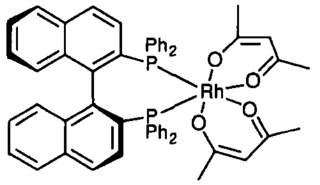
[(*S*)-2,2′-bis(diphenylphosphino)-1,1′binaphthyl]diacetatoruthenium(II) was used as a catalyst in the highly efficient asymmetric hydrogenation of (*E*)- and (*Z*)-phytols [140]. (*S*)-(+)-Ibuprofen was obtained in about 90% ee from 2-(4-isobutylphenyl)-propenoic acid by asymmetric hydrogenation at room temperature and 70 bar dihydrogen pressure in the presence of in situ generated **48** as the catalyst [141].

The catalytic hydrogenation of the mixture of (*E*)- and (*Z*)-**49** in the presence of 1 mol% $Ru(OAc)_2$/(*S*)-BINAP in a 5:1 mixture of ethanol and dichloromethane at 15 °C gave (*R*)-**50** in about 51% ee. The unreacted olefin was found to be the (*E*)-isomer [142].

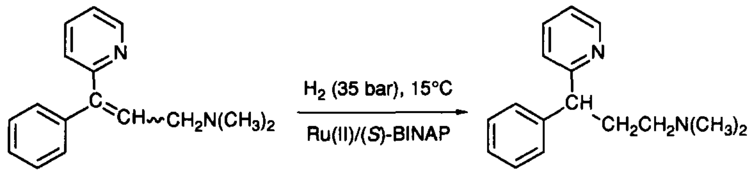
Diketene was enantioselectively hydrogenated to optically active 4-methyloxetan-2-one in up to 97% selectivity and 92% ee using a catalytic system derived from



**45** **46** **47**

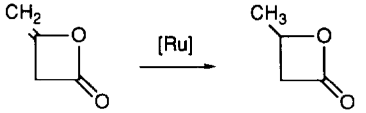


**48**



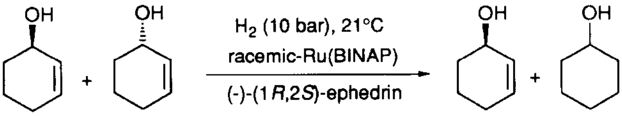
**49** **50**

{RuCl[(*S*)- or (*R*)-BINAP](benzene)}Cl and triethylamine or $Ru_2Cl_4$[(*S*)- or (*R*)-BINAP]$_2$($NEt_3$) in THF [143].



New BINAP-ruthenium(II) complexes were prepared and used as catalysts for the asymmetric hydrogenation of enamides, allylic and homoallylic alcohols, $\alpha,\beta$-unsaturated carboxylic acids, and various functionalized ketones leading to exceptionally high enantiomeric excesses [144].

The kinetic resolution of racemic 2-cyclohexenol has been achieved by hydrogenation using racemic (BINAP)–$RuCl_2(DMF)_x$ as catalyst and deactivating one enantiomer of the catalyst with an enantiomerically pure chiral poison. Thus, poisoning of racemic (BINAP)–$RuCl_2(DMF)_x$ with (1*R*,2*S*)-ephedrine provided (*R*)-2-cyclohexanol in 93% ee at 72% conversion [145].



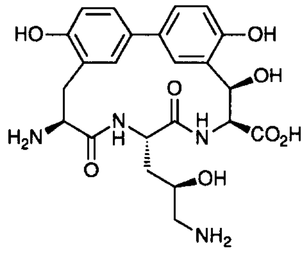
Ruthenium(II)-tetrasulfonated-BINAP was found to be an excellent asymmetric hydrogenation catalyst for 2-acylamino acid precursors and methylenesuccinic acid in both methanolic as well as in neat water solvent systems. Enantiomeric excesses approaching 90% were obtained at room temperature and 1 bar of dihydrogen. The effects of solvent, pressure and the addition of triethylamine on enantioselectivity were studied [146].

The effect of reaction temperature and pressure on the optical yields in homogeneous asymmetric hydrogenation of 2-acrylic acids was studied using rhodium and ruthenium complexes as the catalyst. Comercially feasible processes for the preparation of Naproxen and (*S*)-Ibuprofen were presented [147].

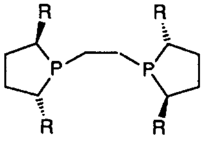
Two of the five sterogenic centers in **51** were formed by enantioselective hydrogenation of the corresponding didehydroamino acids using the rhodium–DIPAMP catalyst and the two sterogenic centers of the $\alpha$-amino-$\beta$-hydroxy unit were created by enantioselective hydrogenation using the ruthenium–BINAP catalyst [148].

Cationic rhodium complexes bearing the new electron-rich $C_2$-symmetric bis(phospholane) ligands **52** and **53** were found to behave as very efficient catalyst precursors for the asymmetric hydrogenation of a broad range of $\alpha$-(*N*-acylamino)acrylate substrates. Enantioselectivities approaching 100% ee were observed in these hydrogenations at 20–25 °C and 2 bar dihydrogen pressure with substrate-to-catalyst ratios of up to 50000 [149].

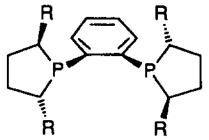
A proposal was made for the geometry of the intermediate responsible for enantioselective hydrogenation of *N*-(acetylamino)cinnamate catalyzed by rhodium complexes containing $C_2$-symmetric diphosphines [150]. The interconversion of the two diastereomeric rhodium(I) complexes — involved in asymmetric hydrogenation —



**51**



**52**



R = Me, Et, Pr, $^{i}$Pr

**53**

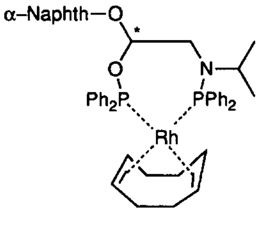
formed from (*S*,*S*)-CHIRAPHOS and methyl (*Z*)-α-acetamidocinnamate was studied with ($^{31}$P, $^{31}$P)-{$^{1}$H}2D EXSY techniques [151].

Ferrocenylalanine was synthesized by asymmetric hydrogenation of the corresponding dehydro acylamino acids at room temperature and 1.1 bar dihydrogen pressure with $[Rh(COD)Cl]_2$/NORPHOS catalyst in up to 95% ee.

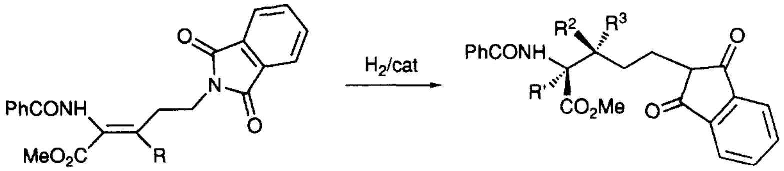
(*Z*)-α-*N*-benzoylamino-β-arylacrylic acids and their esters were hydogenated to the corresponding optically active α-benzoyl-β-arylalanine derivatives with 82–95% ee using the cationic rhodium complex of PROPRAPHOS (**54**) as the chiral catalyst [153].

Stereochemical aspects of the DuPHOS–Rh(I)-catalyzed asymmetric hydrogenation of dehydroamino acids to (*S*)-α-amino acids were studied by NMR examination [154]. Compound **56a** or **56b** was prepared in 60% yield from **55a** or **55b** by asymmetric hydrogenation of deuteration, respectively, catalyzed by (*R*)-Rh–PROPHOS in methylene chloride at 30 °C [155].

The catalytic efficiency of **57** and **58** in asymmetric hydrogenation of (*Z*)-2-acylamino-acrylic acid derivatives in methanol solution at 25 °C and 1 bar $H_2$ was



**54**



**55** a R = H
b R = D

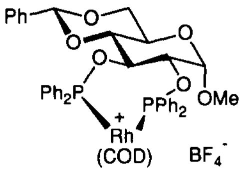
**56** a R' = R$^2$ = D, R$^3$ = H
b R' = R$^2$ = H, R$^3$ = D

evaluated [156]. The variation of the β-aryl aglycone in **59** was found to have little or no effect on the enantioselectivity in the hydrogenation of methyl (Z)-2-acetamidocinnamate [157].

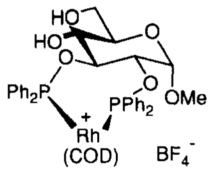
Both activity and enantioselectivity were found to be enhanced significantly in the presence of surfactants in the homogeneous asymmetric hydrogenation of methyl (Z)-α-acetamidocinnamate in aqueous medium using $[Rh(COD)_2]BF_4 + 1.1$ bppm (bppm = (2*S*,4*S*)-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine) as the catalyst system [158].

The rhodium complex of a new chiral 1,3-bisphosphine (1*R*,2*R*)-1-diphenylphosphino-2-(diphenylphosphinomethyl)cyclopentane was found to be one of the most efficient catalysts known for asymmetric hydrogenation of amino acid precursors [159].

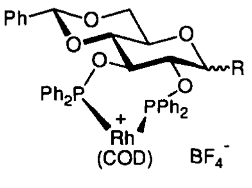
The effects of the diphenylphosphino groups of modified DIOPs **60** on the enantioselectivity and the catalytic activity of their rhodium(I) complexes in the catalytic asymmetric hydrogenations of electron-rich enamides were studied. The cationic rhodium(I) complexes of DIOPs bearing electron-donating groups were found to show higher catalytic activities than that of original DIOP, and the cationic com-



**57**



**58**



R = β-OPh, β-OBn, β-O-2-Naphthyl,
β-O-(4-MeOC$_6$H$_4$), β-O-(4-NO$_2$C$_6$H$_4$),
β-O-(2-MeOC$_6$H$_4$), β-O-(2-NO$_2$C$_6$H$_4$).

**59**

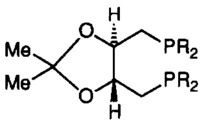
plexes show better enantioselectivities than the corresponding neutral ones. A catalyst with the *p*-methoxy-substituted DIOP ligand was found to be the most efficient [160].

Asymmetric hydrogenation of dimethyl itaconate to dimethyl (*S*)-methylsuccinate was achieved in 49% ee using a racemic catalyst, $[(\text{chiraphos})\text{Rh}]_2(\text{BF}_4)_2$ in the presence of a chiral poison, (*S*)-$[\text{Ph}_2\text{POCH}_2\text{CH}(\text{NMe}_2)\text{CH}_2\text{CH}_2\text{SMe}]$. The origin of the observed effect is attributed to enantioselective poisoning of the active catalyst and chiral amplification resulting from different stabilities of the diastereomeric dimeric prcursors [161].

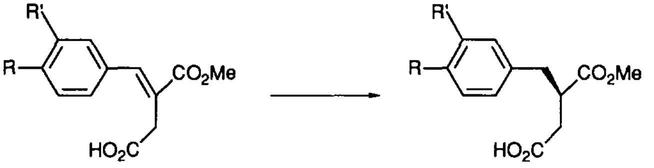
2,6-Dimethyl-L-tyrosine was prepared in kg-scale in high optical purity from the corresponding dehydroamino acid by asymmetric hydrogenation at room temperature and 2 bar $H_2$ in the presence of $[\text{Rh}(1{,}5\text{-COD})(R{,}R\text{-DIPAMP})]\text{BF}_4$ [162].

Optically pure (*R*)-arylmethylsuccinic acid monomethyl esters **61** (R = HO, MeO, R′ = MeO; RR′ = methylenedioxy) were obtained efficiently by using the catalytic asymmetric hydrogenation of the corresponding arylmethylenesuccinic acid monoesters with rhodium(I) complex of the chiral biphosphine **62** [163].

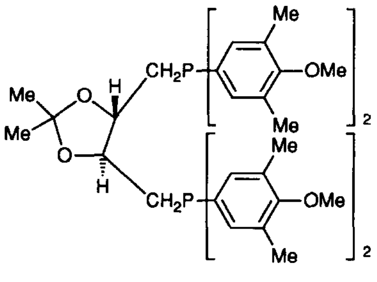
Optical yields of up to 75% were obtained in the rhodium-catalyzed asymmetric



**60**



**61**



**62**

hydrogenation of α-acetamidocinnamic acid and methyl α-acetamidocinnamate using **63** as cocatalyst [164].

Catalytic asymmetric hydrogenation of 2-(acetylamino)acrylic acids and 2-(acetylamino)cinnamic acids in the presence of a rhodium complex with the chiral biphosphine **64** resulted in 54–97% ee. The applied substrate/catalyst ratios were between 250:1 and 11000:1 [165].

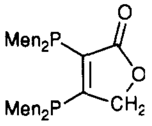
Hydrogenation of (*Z*)-2-*N*-acylamino-3-thienyl-acrylic acids and their esters using **65** and **66** as catalysts gave the corresponding optically active alanine derivative with optical yields up to 90% [166].

The influence of the different protective groups of acylaminocinnamic acid esters on the rate and enantioselectivity of their rhodium-catalyzed asymmetric hydrogenation in the presence of **67**, **68**, **69**, and **70** as chiral ligands were investigated [167].

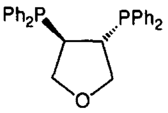
A rhodium complex of sulfonated (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl was used as catalyst in asymmetric hydrogenation of 2-acetamidoacrylic acid and its methyl ester at room temperature under 1 bar $H_2$ in water. Optical yields as high as those obtained in nonaqueous solvent were found [168].

The effect of the symmetry of the chiral rhodium catalyst with **69** and **71** as the ligand in asymmetric hydrogenation of (*Z*)-α-acetamidocinnamic acid on the activity and enantiomeric excess of the product at various pressure was investigated [169].

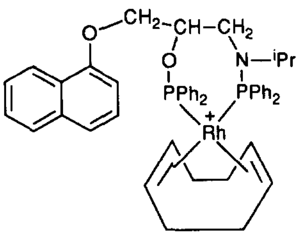
The complexation of *N*-acetyldehydrophenylalanyl-(*S*)-proline with calcium(II)

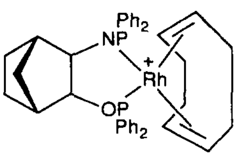


**63**

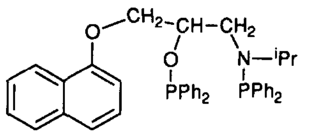


**64**

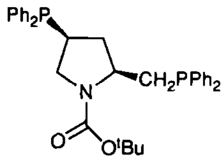




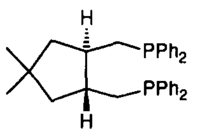
**65** **66**



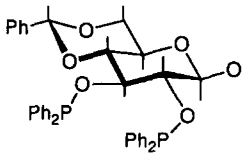
**67**



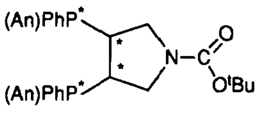
**68**



**69**



**70**



An = 2-methoxylphenyl

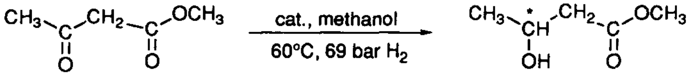
**71**

and nickel(II) ions was found to restrict the conformation of the dehydrodipeptide resulting in a large increase in optical yield during hydrogenation over achiral catalysts [170].

Poly[γ-(L-tyrosinamido)propylsiloxane]-palladium catalyst supported on fused $SiO_2$ was used in hydrogenation of acrylonitrile, acrylic acid, cyclohexene, 1-decene, styrene, and itaconic acid. In the latter case 30% yield of the optically pure product was obtained [171]. See also Ref. [174].

### 3.3.2. *Asymmetric hydrogenation of ketones*

The air-stable BINAP complexes of ruthenium(II), $(RC_5H_4)Ru(S\text{-}(-)\text{-}BINAP)Cl$ ($R = H, CH_3$) were found to be effective homogeneous catalysts for the enantioselective hydrogenation of β-ketoesters [172]. E.g.:

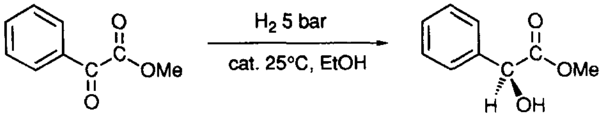


$$CH_3C(=O)CH_2C(=O)OCH_3 \xrightarrow[60°C,\ 69\ bar\ H_2]{cat.,\ methanol} CH_3\overset{*}{C}H(OH)CH_2C(=O)OCH_3$$

≥99% yield and 94% ee of the (+)-izomer

The ruthenium-catalyzed enantioselective hydrogenation of β-keto esters was studied [173]. Asymmetric hydrogenation of carbonyl compounds bearing phenylglyoxyloyl group in the presence of [RuX(*p*-cymene)BICHEP]X (X = I, Cl) and

$Ru(OAc)_2$(BICHEP) (BICHEP = **72**) as the catalyst at 25 °C and 1–40 bar dihydrogen afforded the corresponding alcohol very efficiently. E.g.:



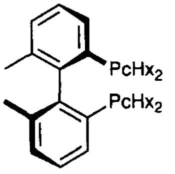
>99% ee

In the presence of the cationic ruthenium complex and $Et_3N$, tiglic acid was smoothly hydrogenated in methanol to (*S*)-2-butyric acid in quantitative yield and >95% ee [174]. The asymmetric hydrogenation of 3,5-dioxo esters $RCOCH_2COCH_2CO_2Me$ (R = Me, Pr, $PhCH_2OCH_2$) using $Ru_2Cl_4$[(*R*)- or (*S*)-BINAP$]_2(NEt_3)$ as the catalyst gave dominantly anti 3,5-dihydroxy esters $RCH(OH)CH_2CH(OH)CH_2CO_2Me$. It was revealed that the hydrogenation proceeds dominantly via the β-diketone mode [175]. The use of BINAP–ruthenium(II) complex in hydrogenation of 2-substituted 3-oxo carboxylic esters allowed selective production of one stereoisomer among four possible isomers. The stereoselectivity obtained by the dynamic kinetic resolution depends on facile in situ racemization of the substrates, efficient chirality recognition ability of the catalysts, and the structures of the ketonic substrates. Quantitative expression of the dynamic kinetic resolution was elaborated [176].

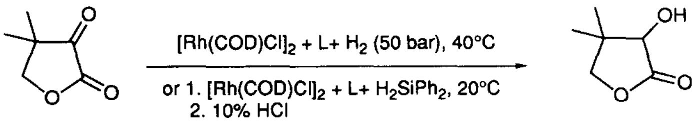
Sugar-derived phosphinites such as **75** or **76** were used as ligands in the catalytic asymmetric hydrogenation or asymmetric hydrosilylation of α-ketopentolactone (**73**), and the best results were 20% or 10% ee of (*R*)-**74**, respectively [177].

Rhodium complexes $[Rh(L_2^*)Cl]_2$ (L = alkylarylamidophosphinephosphinite chelating ligands, such as **77**) were found to be highly effective precursors for the catalytic asymmetric hydrogenation of ketopantoyllactone and benzylphenyl glyoxamide to the corresponding alcohol with 96 and 79.6% ee, respectively [178].

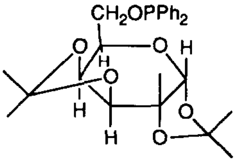
The in situ prepared rhodium complex **78** was found to be an efficient catalyst for



**72**



**73** **74**



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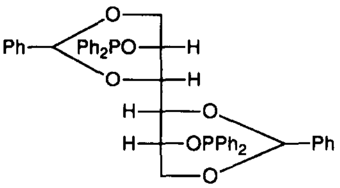
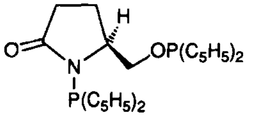


**76**



**77**

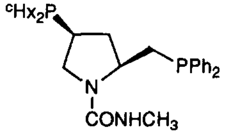
asymmetric hydrogenation of γ-amino ketone-HCl derivatives at 50 °C and 50 bar dihydrogen pressure in methanol in the presence of triethylamine. 100% conversions and the formation of the corresponding alcohols with up to 88.4% ee of *R* configuration were reported [179].

Highly enantioselective hydrogenation of prochiral 1,2-benzocycloalkanones and β-thiacycloalkanones has been achieved by using the new catalytic systems containing of [Ir(BINAP)(COD)]$BF_4$ or [Ir(($H_8$-BINAP)(COD)]$BF_4$ ($H_8$-BINAP = 2,2′-bis(diphenylphosphino)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl) and a mixed P,*N*-donor ligand, bis(*o*-(*N*,*N*-dimethylamino)phenyl)phenylphosphine [180].

Different chiral dithio or azathio ether ligands were tested in the enantioselective reduction of acetophenone into 1-phenylethanol under atmospheric pressure of dihydrogen and room temperature, with palladium(II) chloride or palladium(II) acetate. The influence of the ligand structure on the conversion and on the chemoselectivity of the reaction was studied. Up to 16% ee was observed [181]. See also Refs. [144,148].

### *3.3.3. Asymmetric hydrogenation of imines and oximes*

High diastereoselectivity was observed in hydrogenation of (*R*)-**78** to the corresponding secondary amines using an in situ prepared rhodium-2*S*,4*S*-BDPP catalyst. The rate of hydrogenation of (*R*)-**79** is about 10 times faster than the rate of hydrogenation of (*S*)-**79**. This combined with the high diastereoselectivity of the the



**78**

imine hydrogenation allowed the kinetic resolution of racemic α-methylbenzylamine with 98% ee [182].

### 3.4. Hydrogenation of dienes and alkynes

The catalytic action of binuclear Ti–H complexes on the hydrogenation of diphenylacetylene was examined in order to study the effects of the structures of the catalysts. The binuclear Ti–H complexes also catalyze the hydrogenation of diphenylethylene [183].

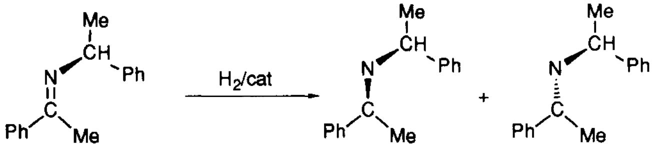
Hydrogenation of diphenylacetylene in the presence of $[Fe_2Ru(CO)_{12}]$, $[FeRu_2(CO)_{12}]$, $[H_2FeRu(CO)_{13}]$, $[H_2Ru_4(CO)_{13}]$ and related complexes has been studied [184]. The cluster complex $[Ru_3(\mu\text{-}H)(\mu^3\text{-ampy})(CO)_8(PPh_3)]$ (Hampy= 2-amino-6-methylpyridine) was found to promote the selective homogeneous hydrogenation of diphenylacetylene to stilbene at 80 °C and 1 bar dihydrogen pressure [185].

Cylododecatriene was hydrogenated to a mixture of *cis*- and *trans*-cyclododecene and cyclododecane at 140 °C and 3 bar dihydrogen pressure in the presence of $Co_2(CO)_6(P^nBu_3)_2$ as the catalyst precursor [186].

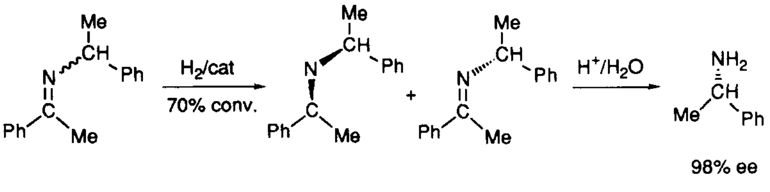
The iridium complex $[Ir(COD)\eta^2\text{-}^iPr_2PCH_2CH_2OCH_3)]BF_4$ was found to be a very active and highly selective catalyst for the hydrogenation of phenylacetylene to styrene at 25 °C and 1 bar dihydrogen pressure. The kinetic and spectroscopic investigations revealed that the hydrido-alkynyl complex $[IrH(C_2Ph)(COD)(\eta^2\text{-}^iPr_2P\text{-}CH_2CH_2OCH_3)]BF_4$ is the main species under catalytic conditions, but the hydrogenation proceeds via the dihydride $[IrH_2(COD)(\eta^2\text{-}^iPr_2PCH_2CH_2OCH_3)]BF_4$ and the β-phenylvinyl-intermediate $[IrH(CH{=}CHPh)(COD)(\eta^2\text{-}^iPr_2PCH_2CH_2OCH_3)]BF_4$ [187].

In the hydrogenation of phenylacetylene by $PdCl_2$ and 5% $Pd/Al_2O_3$, $[PdCl_2(PhC{\equiv}CH)]_2$ and $Pd(PhC{\equiv}C)_2(PhC{\equiv}CH)_2$, respectively, have been identified by IR and UV/Vis spectroscopy [188].

The kinetics and mechanism of acetylene hydrogenation catalyzed by gold tri-



79 333 : 1



chloride-potassium tetrahydroborate-water system was studied between 17 and 30 °C [189]. See also Refs. [133,195,236].

### 3.5. Hydrogenation of arenes and heterocyclic compounds

Ytterbium grafted onto $SiO_2$ or $Al_2O_3$ in the form of $\equiv$CSi–O–Yb–$NH_2$ or $=$Al–O–Yb–$NH_3$ groups, respectively, was found to be a catalyst for the partial hydrogenation of benzene to cyclohexene at 25 °C with extreme high selectivity of 96–100% [190].

Silica supported group 5 metal organometallic compounds, $[(Me_3SiCH_2)M(\mu\text{-}CSiMe_3)_2M(CH_2SiMe_3)_2]$ (M = Nb, Ta) were applied for the exhaustive hydrogenation of a variety of aromatic substrates at 120 °C and 83–97 bar dihydrogen pressure [191].

The hydrogenation activity of $Li[AlH_n(OR)_{4-n}]/CoBr_2$ systems in anthracene hydrogenation was studied at 25 °C and atmospheric pressure [192]. In particular, the system $Li[AlH(O\text{-}^tBu)_3]/CoBr_2$ in THF was found to be a very active catalyst for the hydrogenation of anthracene at 25 °C [193].

The kinetics and mechanism of the regiospecific homogeneous hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline using $[Rh(COD)(PPh_3)_2]PF_6$ as the catalyst precursor in toluene solution between 59 and 97 °C at 1 bar dihydrogen pressure were studied. The rate low for the hydrogenation was found to be $-d[\text{quinoline}]/dt = k_{cat}\,[Rh][H_2]^2$ [194]. Anthranilato- and *N*-phenylanthranilato-rhodium(I) complexes containing triphenylphosphine ligands were found to be active in hydrogenation of some alkanes, dienes, aromatic and heteroaromatic compounds [195]. $[Rh(I)PPh_3]^+$/montmorillonite was found to catalyze the hydrogenation of benzene to cyclohexane at 70 °C and 20 bar dihydrogen pressure [196].

Benzo[b]thiophene complexed to triphos iridium was hydrogenated in homogeneous solution at 20 °C or in the solid state at 80 °C at 5 bar dihydrogen pressure as a model reaction for hydrodesulfurization [197].

Benzene hydrogenation using a homogeneous catalyst prepared from organic acid nickel salt, alkylaluminium, weak organic acid, and water was studied [198].

### 3.6. Hydrogenation of carbonyl compounds

The kinetics of hydrogenation of acetophenone in the presence of dimolybdenum tetraacetate as the catalyst were studied. The reaction was found to be first-order each in catalyst and dihydrogen partial pressure and zero-order in acetophenone in the concentration range of 2.1 and 6.5 M [199].

A new and effective method was described for the synthesis of sorbitol in 95% yield by catalytic hydrogenation of glucose at 90 °C and 2 bar dihydrogen pressure using $RuCl_3$–$2PPh_3$ as the catalyst [200]. D-Fructose was hydrogenated to a 1:1 mixture of D-glucitol and D-mannitol at 100 °C and atmospheric pressure using $RuCl_2(PPh_3)_3$ as the catalyst. Besides hydrogenation, fructose undergoes transfer hydrogenation when propan-2-ol and butan-2-ol are used as solvent. The rate of hydrogenation was found to be comparable with transfer hydrogenation under similar reaction conditions [201].

The selective hydrogenations of $\alpha,\beta$-unsaturated aldehydes (3-methyl-2-butenal, all-*trans*-retinal and hydroquinone all *trans*-retinal complex) into allylic alcohols, were studied using $RuCl_2(TPPTS)_3/SiO_2$ (TPPTS = tris(*m*-sulfophenyl)-phosphine trisodium salt), $RuH_2(TPPTS)_n/SiO_2$ and supported phosphino-iridium catalysts [202].

The water soluble ruthenium complex *cis*-$[Ru(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$, ($6,6'\text{-}Cl_2bpy$ = 6,6′-dichloro-2,2′-bipyridine) was found to be an effective catalyst for the hydrogenation of organic carbonyl compounds (e.g.: acetophenone, benzaldehyde) and olefins (for example: 1-octene, styrene) in biphasic aqueous/organic systems. The complex catalyzed the H/D exchange reaction between $H_2$ and $D_2O$ and incorporation of deuterium into the hydrogenation product of acetophenone was observed in catalysis performed in a $D_2O$/cyclohexane biphasic medium [203].

Ruthenium(III) chloride bound on functionalized polymers containing N–P, N–O, or N–N binuclear ligand sites was used in the hydrogenation of diacetone alcohol [204]. See also Refs. [92,133,236].

### 3.7. *Hydrogenation of nitro compounds*

A rhenium complex was used in catalytic hydrogenation of *m*-, *p*-, and *o*-nitrobenzoic acids to the corresponding amino benzoic acids [205]. Rhenium complexes having $Re_3S_7$ and $Re_3S_4$ clusters were studied as catalysts in the hydrogenation of *m*-nitrobenzoic acid. Complexes containing the $Re_3S_7$ cluster surrounded by hydroxo groups were found to show the highest activity [206].

The poly-$\omega$-(aminoethylamino)undecylsiloxane palladium complex was found to display high activity for the hydrogenation of styrene, acrylonitrile, and nitrobenzene in ethanol at 40 °C under an atmospheric pressure of dihydrogen. The palladium complex is air stable and can be easily recovered and reused [207]. See also Ref. [133].

### 3.8. *Miscellaneous hydrogenations*

The catalytic hydrogenation of nitriles in methylene chloride in the presence of cationic iridium–triphenylphosphine complexes gave HCl salts of primary and secondary amines [208].

### 3.9. *Dehydrogenation*

The zirconocene complex $Cp_2^{*}Zr(Si(SiMe_3)_3)Me$ was found to catalyze the dehydrogenative coupling of ((trifluoromethyl)phenyl)silanes to poly[((trifluoro–methyl)-phenyl)silane] [209].

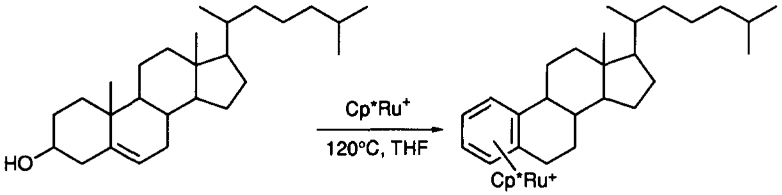
Tungsten(VI) hexahydride and rhenium(V) pentahydride complexes, supported by the chelating triphosphine ligand $PPh(CH_2CH_2PPh_2)_2$, were found to be active catalysts for the thermal dehydrogenation of cyclooctane to cyclooctene at 145 and 185 °C, respectively in the presence of *tert*-butylethylene [210].

A variety of homogeneous catalysts such as $[PhP(CH_2CH_2PPh_2)_2WH_6]$, $[PhP(CH_2CH_2PPh_2)_2ReH_5]$, and $[IrH_2(O_2CC_2F_5)(P(^cHx)_3)_2]$ were studied for cyclooctane dehydrogenation activity under reflux [211]. A series of trimethylphosphine or triphenylphosphine ligand-containing rhenium complex catalysts were tested with respect to their activity in dehydrogenation of cyclohexane and cyclooctane at 80–100 °C in the presence of *tert*-butylethylene as hydrogen acceptor [212].

Evidence for the formation of 1,3,5-trisilabenzene was obtained by hydrogen elimination during the metal ion-catalyzed dehydrogenation of 1,3,5-trisilacyclohexane in the gas phase. Metal ions found to catalyze this dehydrogenation include $Fe^+$, $Co^+$, $Ni^+$, $CpFe^+$, $CpCo^+$ and $CpNi^+$ [213].

Photolysis of $[(\pi\text{-}C_5R_5)Ru(MeCN)_3]^+$ (R = H, Me) with cyclohexane, cyclohexene, 2-cyclohexen-1-one, or 3-methyl-2-cyclohexen-1-one in methylene chloride afforded $[(\pi\text{-}C_5R_5)Ru(\pi\text{-}C_6H_5R'C)]^+$ (R'C = H, Me) in 10–40% yields [214].

Selective near-quantitative aromatization of the A-ring of steroids (testosterone, progesterone, cholesterol, dehydroisoandrosterone, or androsterone) through C–C, C–H, and C–O bond activation by the $Cp^*Ru^+$ fragment generated by the protonation of $[Cp^*Ru(OMe)]_2$ by $CF_3SO_3H$ afforded $\eta^6$-aryl derivatives at 90–120 °C in THF and $CH_4$, $H_2$ and/or $H_2O$ as byproducts [215]. E.g.:



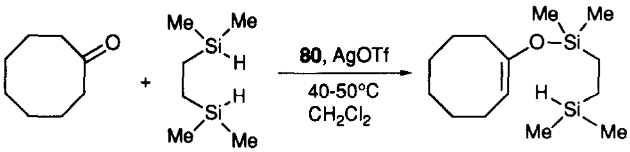
100% spectroscopic yield

Thermo- and photocatalytic dehydrogenation of 2-propanol with $[RuCl(SnCl_3)_5]^{4-}$ or $[Ru(SnCl_3)_6]^{4-}$ complexes was investigated. The observed kinetic isotope effects for 2-propanol-2-$d_1$ at 82.4 °C indicate that the step involving C–H bond splitting at the methine group is rate-determining. The activation energies were found to be 113 and 21 KJ $mol^{-1}$ under dark and photoirradiation conditions, respectively [216].

The effect of carbon monoxide pressure between 0 and 600 mmHg on the nature of the active centers in the photocatalytic dehydrogenation and carbonylation of pentane in the presence of bis(trimethylphosphine)carbonylrhodium(I) chloride was investigated [217].

The photocatalysis of cyclooctane dehydrogenation by the A-frame dinuclear rhodium complex $[Rh_2(\mu\text{-}S)(CO)_2(dppm)_2]$ (dppm = bis(diphenylphosphino)methane) was studied. Irradiation at 475 nm caused dehydrogenation of cyclooctane with 32.8 $h^{-1}$ initial turnover frequency and 27.3 total turnover numbers [218].

The dehydrogenative silylation of ketones with 1,2-bis(dimethylsilyl)ethane to the corresponding silylenol ether was found to be catalyzed by a mixture of **80** and AgOTf. E.g.:

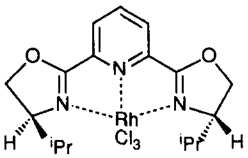


$Rh(P^iPr_3)_2Cl$ was found to dehydrogenate cyclooctane to give $H_2Rh(P^iPr_3)_2Cl$ and cyclooctene. Using norbornene as a hydrogen acceptor, catalytic transfer-dehydrogenation was observed [220]. The thermocatalytic dehydrogenation of cyclo- and *n*-alkanes with $Rh(PR_3)_3Cl$ (R = aryl or alkyl) under boiling and refluxing conditions was reported. In the presence of hydrogen acceptors such as alkenes, hydrogen transfer rather than dihydrogen evolution occured [221].

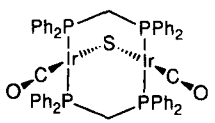
Catalytic cyclooctane photodehydrogenation at unusually low photon energy was observed in the presence of **81** [222].

The dehydrogenative double silylation of acetylenes with *o*-bis(dimethylsilyl)benzene was catalyzed by $Pt(CH_2{=}CH_2)(PPh_3)_2$ under mild conditions to give **82** in 50–100% yields. Dependent on the structure of the acetylene **83** and **84** were also formed as byproducts. The selectivity trend for acetylenes undergoing dehydrogenative double silylation was internal acetylenes > mono-substituted acetylene-unsubstituted acetylenes [223].

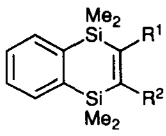
Five-coordinated platinum complexes, $[Pt(SnCl_3)_2(P(OR)_3)_3]$ were found to be



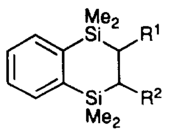
**80**



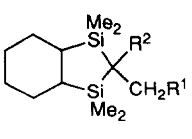
**81**



**82**



**83**



**84**

($R^1$,$R^2$ = H,H; n-hexyl, H; Ph, H; Pr, Pr; Ph,Ph; $CO_2Me$, $CO_2Me$

active catalysts for dehydrogenation of cyclooctane in homogeneous solutions under mild reaction conditions [224]. See also Ref. [630].

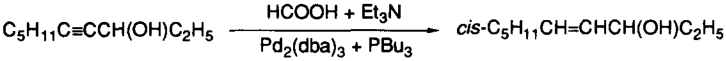
### *3.10. Hydrogen transfer reactions (organic compounds as reductants)*

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

Phosphinatoirons were found to promote the reduction of alkenes and alkynes with $NaBH_4$ in benzene-ethanol. Styrene gave 2,3-diphenylbutane (*meso* and ±) and ethylbenzene in 13 and 76% yield, respectively by using $(ClTPP)Fe^{III}Cl$ (ClTPP = 5,10,15,20-tetrakis(*p*-chlorophenyl)porphyrin dianion) as the catalyst [225].

The mechanism of the rhodium-catalyzed enantioselective transfer hydrogenation of itaconic acid and related $\alpha,\beta$-unsaturated carboxylic acids using formic acid/triethylamine (5:2) as the hydrogen source was investigated. Decarboxylation of a transient formate species to form hydridic complexes of rhodium was suggested to be involved [226].

Transfer hydrogenation of alkynes using formic acid/triethylamine as a hydrogen source in the presence of a palladium(0)-catalyst was found to afford *cis*-alkenes highly stereoselectively in excellent yields [227]. E.g.:



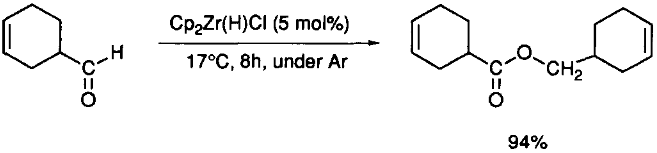
$$C_5H_{11}C{\equiv}CCH(OH)C_2H_5 \xrightarrow[Pd_2(dba)_3\,+\,PBu_3]{HCOOH\,+\,Et_3N} cis\text{-}C_5H_{11}CH{=}CHCH(OH)C_2H_5$$

See also Refs. [220,221,236,275].

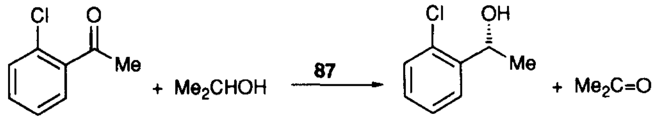
#### *3.10.2. Transfer hydrogenation of ketones and aldehydes*

The Meerwein–Ponndorf–Verley reduction of **85** in the presence of 5 mol% catalyst **87** by 2-propanol at 25 °C was found to afford **86** in 97% ee and 96% yield. The effect of lanthanide metal size on the enantioselectivity of the reduction of *o*-chloroacetophenone reduction was also investigated. The corresponding Nd, Sm, and Tb complexes show optimum selectivities. Diminished enantioselectivities and reduced catalytic activity was found in the case of either larger or smaller lanthanide ionic radii [228].

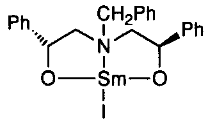
Zirconium tetra-*i*-propoxide was found to catalyze the reduction of various aldehydes and ketones with 2-propanol to the corresponding alcohols in high yields [229]. Zirconocene and hafnocene complexes such as $Cp^{*}_{2}MH_2$ and $Cp^{*}_{2}M(Cl)H$ (M = Zr or Hf) were found to catalyze the selective dimerization of aldehydes to esters under mild reaction conditions [230]. E.g.:



The nonclassical trihydrides $[(PP_3)M(H)(\eta^2\text{-}H_2)]BPh_4$ ($PP_3 = P(CH_2CH_2PPh_2)_3$; M = Fe, Ru, Os) were found to be efficient catalyst precursors for the reduction of

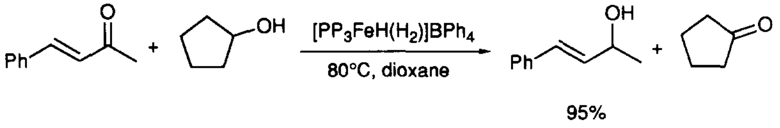


**85** **86**



**87**

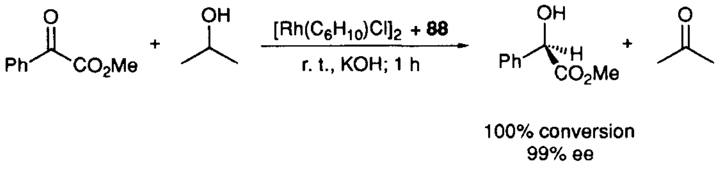
$\alpha,\beta$-unsaturated ketones to unsaturated alcohols via hydrogen-transfer from secondary alcohols [231]. E.g.:



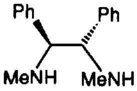
The effect of microwave heating on the catalytic activity of the RuHCl(CO)(PPh$_3$)$_3$ catalyzed transfer hydrogenation of benzaldehyde in which formic acid serves as the hydrogen donor was examined. Carrying out the reaction in a household microwave oven produced an improvement in the average catalytic turnover rate from 280 to 6700 turnovers per hour in comparison with traditional reflux heating [232].

The catalytic activity of MH($\eta_2$-O$_2$CR*)(CO)(P(CHMe$_2$)$_3$)$_2$ (M = Os, Ru; R* = (*S*)-CH(NaphOMe)Me, (*R*)-CH(OMe)Ph, (*R*)-CCF$_3$(OMe)Ph in asymmetric hydrogen transfer fromisopropanol to acetophenone was studied. The osmium carboxylates lead to considerably higher optical yields than the ruthenium complexes [233].

The catalytic enantioselective reduction of various prochiral ketones using $C_2$-symmetric diamines as ligands of rhodium was investigated. The best results were obtained with diamine **88** [234]. E.g:



Hydrogen-transfer reaction from 2-propanol to aliphatic and aromatic ketones, $\alpha,\beta$-unsaturated ketones, keto esters, aldehydes and nitriles, catalyzed by Ir(PNP)($\sigma,\eta^2$-C$_8$H$_{13}$) (PNP = PrN(CH$_2$CH$_2$PPh$_2$)$_2$) was reported [235]. The complex IrCl$_2$H(P$^i$Pr$_3$)$_2$ in the presence of NaBH$_4$ was found to catalyze hydrogen



**88**

transfer from 2-propanol to cyclohexanone, 3-methylcyclohexanone, benzylideneacetone, styrene, and cyclohexadienes. The complex $IrCl_2H(P^iPr_3)_2$ was found to be an active catalyst for the hydrogenation of unsaturated substrates [236]. See also Ref. [201].

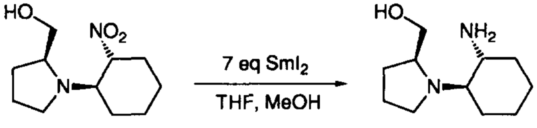
### 3.10.3. Transfer hydrogenation of miscellaneous organic compounds

Nitrobenzene was selectively reduced to aniline by aqueous methyl formate in the presence of a catalytic system comprising $Ru_3(CO)_{12}$, $Pd(OAc)_2$, tricyclohexylphosphine, and 1,10-phenanthroline [237]. See also Ref. [235].

## 3.11. Reduction without molecular hydrogen

### 3.11.1. Stoichiometric reduction with low-valent transition metal complexes

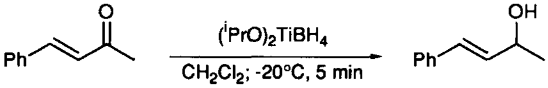
The reaction of benzaldehyde with $SmI_2$ in THF gave *dl*- and *meso*-hydrobenzoin in a 1 : 1 ratio [238]. Thermally labile 2-aminonitroalkanes were reduced stereoselectively by samarium diiodide to give the corresponding 1,2-diamines [239]. E.g.:



90% yield

Samarium dibromide was found to be a powerful one electron reductant able to very efficiently mediate pinacolic couplings [240].

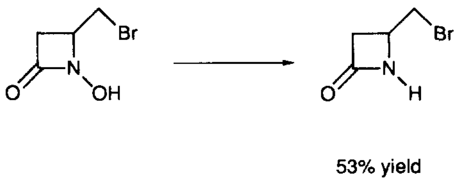
Diisopropoxytitanium(III) tetrahydroborate formed by the reaction of diisopropoxytitanium dichloride and benzyltriethylammonium borohydride (1 : 2) was found to react with a variety of $\alpha,\beta$-unsaturated carbonyl compounds in dichloromethane at $-20\,°C$ to yield exclusively the corresponding allylic alcohols in excellent yields [241]. E.g.:



97% yield

The reductions of aromatic alcohols, aldehydes, ketones, acetals, and ketals with $CpTiCl_3$–$LiAlH_4$ were reported. Thus, the reduction of benzaldehyde gave 75% toluene and 25% benzylalcohol [242].

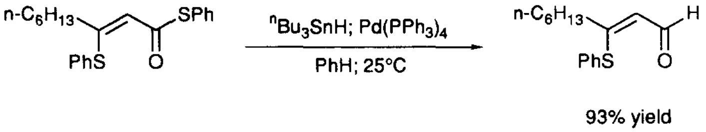
Various *N*-hydroxy-2-azetidinones were reduced to the corresponding *N*-unsubstituted-2-azetidinones with a mixture of $Mn(OAc)_3 \cdot 2H_2O$ and $Cu(OAc)_2 \cdot H_2O$ in ethanol at 55 °C [243]. E.g.:



### 3.11.2. Inorganic or organic reductants in the presence of transition metal complexes

The reduction of *gem*-dichlorocyclopropanes with anthracene anion radicals was found to be accelerated by Co(II) and Ni(II) ions [244].

(*Z*)-1,3-Bis(arylthio)-2-alken-1-ones were chemoselectively reduced to the corresponding aldehydes by $^nBu_3SnH$ with the aid of $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, or $Pd(OAc)_2$ catalysts at room temperature [245]. E.g.:

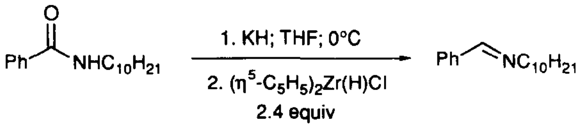


The role of transition metal complexes and solvents in the reduction of trityl halides with alkylmagnesium halides was studied. It was found that in a mixture of benzene and triethylamine, reduction of trityl bromide can proceed in the presence of methylmagnesium iodide [246].

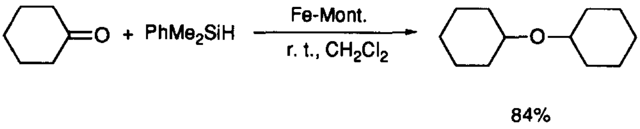
### 3.11.3. Reduction via hydrosilylation

The procedure for the conversion of esters to alcohols using $HSi(OEt)_3$ as the stoichiometric reductant and $Ti(O^iPr)_4$ as the catalyst (S.C. Berk and S.L. Buchwald, J. Org. Chem., 57 (1992) 3751) can become hazardous because highly pyrophoric $SiH_4$ gas can be formed by $Ti(O^iPr)_4$-catalyzed $HSi(OEt)_3$ disproportionation even in the absence of substrate [247].

Hydrogenation of buckminsterfullerene $C_{60}$ to $C_{60}H_2$ was achieved via hydrozirconation with $(\eta^5\text{-}C_5H_5)_2Zr(H)Cl$ [248]. Zirconated amides were transformed by $(\eta^5\text{-}C_5H_5)_2Zr(H)Cl$ to *N*-substituted imines [249]. E.g.:

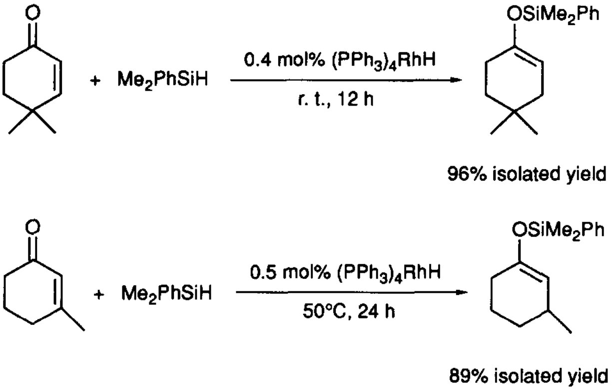


Reduction of carbonyl compounds with hydrosilanes were performed on the surfaces of solid acids and bases [250]. E.g.:



(Fe-Mont. = acidic iron-ion exchanged montmorillonite)

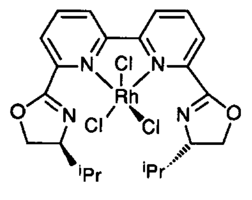
Hydridotetrakis(triphenylphosphine)rhodium(I) was found to act as an effective catalyst for the reactions of α,β-unsaturated carbonyl compounds with silanes to give regioselectively the enol silyl ethers in a 1,4-hydrosilation [251]. E.g.:



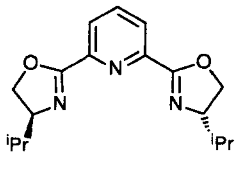
The asymmetric reduction of acetophenone with diphenylsilane in the presence of catalitic amounts of **89** gave (*S*)-1-phenylethanol in 90% ee. The results of asymmetric reductions using rhodium complexes with ligand **90** and **91** were also reported [252].

The reduction of 2,2,4,4-tetramethyl-1,3-cyclobutanedione (**92**) with alkyl- and arylsilanes, catalyzed by a variety of rhodium(I) complexes was studied. The selectivity of the reaction was found to depend strongly on the steric requirements of the silane molecules. Thus, diphenylsilane and amylsilane are selective in the formation of isomeric diols, diphenylsilane favoring formation of the *cis*-diol **93**, and amylsilane yielding mainly the *trans*-diol **94** [253].

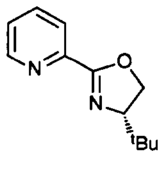
The hydrodesulfurization of dibenzothiophene into biphenyl has been achieved in toluene solution by the reaction with tris(triethylphosphine)platinum(0) and then with $Et_3SiH$ [254]. The platinum(II)-catalyzed hydrosilylation of acetophenone with $MeSiHCl_2$ or $MeSiPh_2H$ was studied [255]. See also Ref. [177].



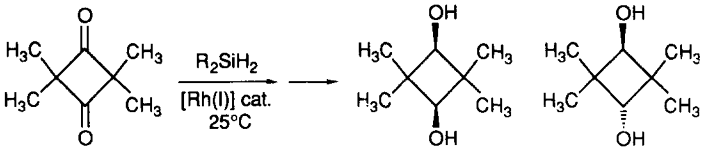
**89**



**90**



**91**



92 93 94

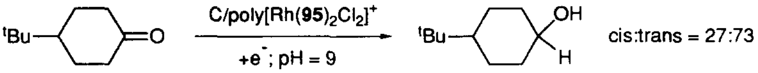
### 3.11.4. Electroreduction and photoreduction

Aldehydes were hydrogenated to the corresponding alcohol with sodium formate in aqueous methanol at 60 °C when photolyzed in the presence of a catalytic amount of $Cr(CO)_6$ [256].

$Re(bpy)(CO)_3Br$ and $Re(terpy)(CO)_3Br$ (bpy = 2,2′-bipyridine; terpy = 2,2′ : 6′C,2″-terpyridine) complexes incorporated into a coated Nafion membrane were found to catalyze the electrocatalytic reduction of $CO_2$ in water to produce formic acid and CO [257]. Controlled potential electrolysis of $[Ru(bpy)(terpy)(CO)]^{2+}$ at −1.70 V vs. $Ag/Ag^+$ in $CO_2$-saturated ethanol:water = 8:2 (v/v) at −20 °C was found to produce not only HCOOH and CO but also formaldehyde, methanol, H(O)CCOOH, and $HOCH_2COOH$ [258].

Benzal chloride was converted to a mixture of *cis*- and *trans*-stilbene by electrogenerated cobalt(I)(salen) [259]. In a mechanistic investigation it was shown that the process involves a sequence involving electrocatalytic conversion of benzal chloride to a mixture of the stereoisomeric 1,2-dichloro-1,2-diphenylethanes, followed by electrocatalyzed conversion of the latter to *cis*- and *trans*-stilbene [260].

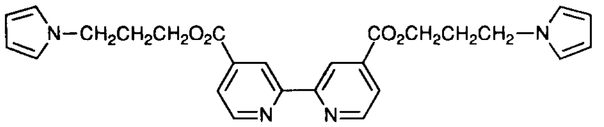
Electrocatalytic hydrogenation of carvone and some substituted cyclohexanones on a rhodium complex-polypyrrole film electrode was reported. E.g.:



100% yield
50% current efficiency

An opposite selectivity was found for the hydrogenation of bulky substrates on the catalytic cathode, as compared with their catalytic or electrocatalytic hydrogenation with similar complexes used in homogeneous media [261].

Electrochemical reduction of nickel(II)(salen) in the presence of benzal chloride in dimethylformamide at a carbon cathode was found to result in catalytic conversion



95

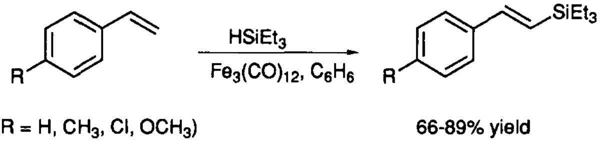
of benzal chloride into toluene, bibenzyl, and trans-stilbene. Depending upon experimental conditions the formation of a variety of other monomeric and dimeric products was also observed [262].

### 3.12. Hydrosilylation and related hydrometalation reactions

Hydrozirconation of various vinyl-borabicyclo[3.3.1]nonanes with $(\eta^5\text{-}C_5H_5)_2Zr(H)Cl$ at 0 °C was reported [263]. Diorganomagnesium compounds were prepared in high yields by the zirconium tetrahalide-catalyzed hydromagnesation reaction of 1-alkenes with in situ prepared magnesium hydride [264]. Hydrozirconation of **96** and **98** with $(\eta^5\text{-}C_5H_5)_2Zr(H)Cl$ gave **97** and **99**, respectively [265].

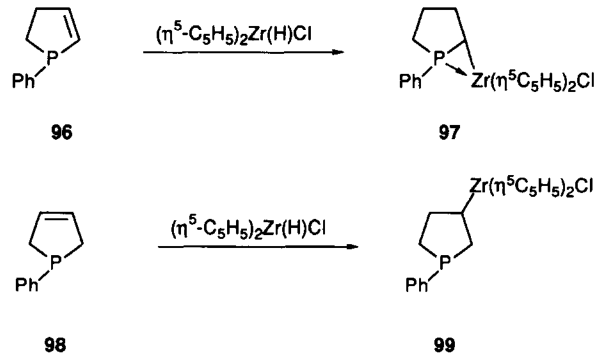
The photocatalyzed hydrosilylation of 1,3-butadiene by triethylsilane in the presence of $Cr(CO)_6$ and $Mo(CO)_6$ was found to yield exclusively *cis*-1-(triethylsilyl)-2-butene [266]. The mechanism of the catalytic hydrosilation of ethylene by $Cp_2^*Ta(\mu\text{-}CH_2)_2Ir(CO)_2$ has been studied [267].

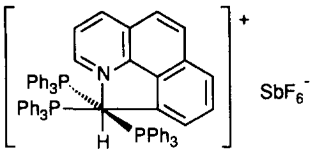
The reaction of styrenes with triethylsilane in the presence of $M_3(CO)_{12}$ (M = Fe, Ru, Os) as the catalyst was examined. Completely selective dehydrogenative silylation was found in the case of $Fe_3(CO)_{12}$ between 40 and 80 °C [268]. E.g.:



The hydrosilylation of 1-octene and acetophenone with $(EtO)_3SiH$ in the presence of $Ru_3(CO)_{12}$ as the catalyst was studied in benzene-dioxane at 50–70 °C [269]. $RuHCl(CO)(P^iPr_3)_2$ was found to be very active and highly selective catalyst for the addition of triethylsilane to phenylacetylene. The reaction leads to *cis*-$PhCH{=}CH(SiEt_3)$ with a selectivity of 100% [270].

The mechanism of a cobalt(III)-catalyzed olefin hydrosilation reaction was investigated. Direct evidence for silyl migration pathway was obtained [271].

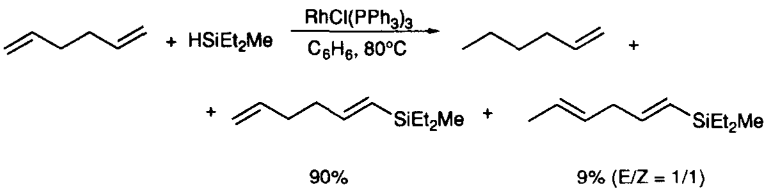




**100**

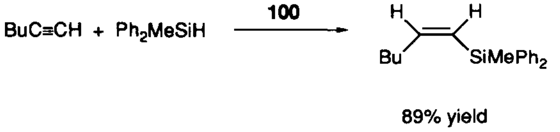
The hydrosilylation of allyl chloride with trimethoxysilane was examined in the presence of several Ir, Co, Pt, and Ru complex catalysts. Ruthenium and iridium complexes exhibit the highest selectivities to give 3-chloropropyltrimethoxysilane [272]. Hydrosilylation of phenylacetylene with $HSiCl_3$, $MeSiHCl_2$, $EtSiHCl_2$, $Me_2SiHCl$, $Et_3SiH$, or $(EtO)_3SiH$ occurred in the presence of heterometallic carbido carbonyl clusters such as $[Me_4][RhFe_5C(CO)_{16}]$. Nearly a 1:1 ratio of *trans*- and *cis*-$PhCH{=}CHSiR_3$ was formed [273].

$[Rh(COD)Cl]_2$-catalyzed hydrosilylation of 1-hexyne with $Et_3SiH$ in EtOH or DMF was found to be highly selective for the formation of (*Z*)-vinylsilane, whereas in acetonitrile in the presence of $PPh_3$ (*E*)-vinylsilane was obtained selectively [274]. The reaction of 1,5-dienes with hydrosilanes in the presence of $RhCl(PPh_3)_3$ as a catalyst gave instead of the usual hydrosilylation products 1-silyl-1,5-dienes as the result of dehydrogenative silylation [275]. E.g.:



The hydrosilylation of (phenylmethylene)cyclopropane with triethylsilane in the presence of $RhCl(PPh_3)_3$ as the catalyst was found to afford $Et_3Si(CH_2)_2CH{=}CHPh$ in 95% overall yield as a nonstereospecific 4:1 mixture of *trans*:*cis* isomers [276].

Di-$\mu$-chlorotetrakis($\eta^2$-methylenecyclopropane)dirhodium(I) was found to be a more active catalyst for the hydrosilylation of alkenes and alkynes than either a similar ethene complex or $RhCl(PPh_3)_3$ [277]. Alkyne hydrosilylation has been examined using $RhCl(PPh_3)_3$ and **100** as the catalyst. The iridium complex **100** was found to be a good catalyst for the anti-addition of silanes to alkynes. $RhCl(PPh_3)_3$ proved to be less selective [278]. E.g.:



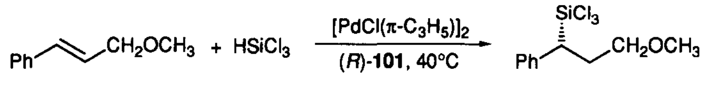
The regio- and stereoselective intermolecular hydrosilylation of allyl alcohols and allylamines catalyzed by platinum and rhodium complexes were studied by deuterium-labeling [279].

The effect of substituents at silicon on the products of hydrosilylation of vinylsilanes catalyzed by nickel acetylacetonate was studied [280]. A systematic investigation of the effects of concentration and properties of tertiary phosphines on the chemoselectivity of hydrosilylation of phenylacetylene with triphenylsilane using nickel(0) catalyst revealed that hydrosilylation is enhanced when the phosphorous ligand is either more basic or less basic than triphenylphosphine. Thus, it was found that tertiary *n*-alkyl- and *n*-alkoxyphosphines using a ligand/metal ratio 2/1 in the presence of $HSiPh_3/PhC{\equiv}CH = 2/1$ afford 85–90% yield of hydrosilylation products [281].

Reaction of simple terminal alkenes $RCH{=}CH_2$ (R = butyl, *n*-hexyl, *n*-decyl, $PhCH_2CH_2$, cyclohexyl) with trichlorosilane at 40 °C in the presence of 0.1 or 0.01 mol% of palladium catalyst prepared from $[PdCl(\pi\text{-}C_3H_5)]_2$ and (*S*)-**101** was found to proceed with unusual regioselectivity (up to 94%) and with high enantioselectivity to give high yields of 2-(trichlorosilyl)alkanes together with a minor amounts of 1-(trichlorosilyl)alkanes. Oxidation of the carbon–silicon bond gave optically active alcohols $RCH(OH)CH_3$ with enantiopurity ranging between 94 and 97% ee [282].

The catalytic activity of palladium triphenylphosphine, trialkylphosphine, and acetylacetonate complexes was studied for hydrosilylation of acetylene with $Cl_3SiH$, $MeCl_2SiH$, $EtCl_2SiH$, $Et_3SiH$, and $(EtO)_3SiH$ in xylene at 70–80 °C to the corresponding vinylsilanes and 1,2-disilylethanes [283].

Asymmetric hydrosilylation of dihydrofuran derivatives with trichlorosilane in the presence of 0.1 mol% $[PdCl(\pi\text{-}C_3H_5)]_2$ and 0.2 mol% (*R*)-**101** at 40 °C gave the corresponding hydrosilylation products of up to 95% ee [284]. Hydrosilylation of styrenes with trichlorosilane between 5 and 40 °C using an in situ prepared palladium complex with (*R*)-**101** gave high yields of optically active 1-aryl-1-silylalkanes (80–85% ee) as single regioisomer [285]. E.g.:

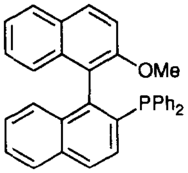


94% yield, 80% ee

*trans*-$PtCl_2(L\text{-}Se)_2$ (L = 10-selenabenzo-15-crown-5) was found to be an efficient catalyst for the hydrosilylation of olefins by $HSi(OEt)_3$. Turnover numbers as high as 62000 were observed [286].

The zwitterionic $\pi$-complexes of platinum, $[Bu_3P^+CH_2CH{=}CH_2][PtBr_3^-]$, $[Bu_3P^+CH_2CH{=}CH_2][PtCl_3^-]$, and $[Bu_3P^+CH_2CH{=}CH_2][(Me_2SO)PtBr_2^-]$-$[Br^-]$ were used as catalysts for hydrosilylation of olefins (1-heptene and styrene) and ketones [287]. The catalytic behaviour of a platinum complex of a new type of crown ether functionalized polysiloxane has been studied in the hydrosilylation of olefins with triethoxysilane [288].

Silica supported platinum complexes with dithiacrown ether groups were found to be effective catalysts for the hydrosilylation of olefins with triethoxysilane [289].



**101**

The effect of ligands in $[Pt(Ph_3E)_2X_2]$ (E = P, As, Sb; X = Cl, I, $NO_2$, SCN, $1/2SO_3$) in hydrosilylation of 1-heptene by $MeSiCl_2H$ was studied [290].

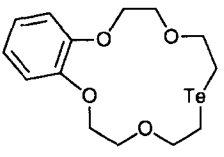
Hydrosilylation of 1-decene with triethoxysilane in the presence of a platinum complex with **102** as a ligand gave 1-[(triethoxy)silyl]decane in 55% yield [291].

Mesitylene solvated platinum atoms were used as alkyne and conjugated diene hydrosilylation catalysts between 25 and 80 °C [292]. Platinum complexes having the formula RPtX, where R is an organic or organosiloxane species containing $\geqslant 2$ unsaturated fragments and X is a halogen, preferably chlorine, were found suitable as catalyst for the preparation of organosilicon resins by hydrosilation [293].

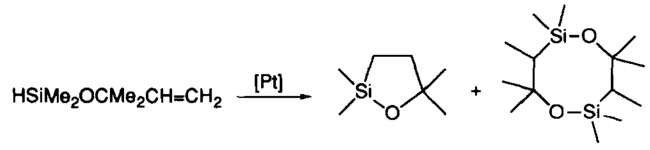
Cyclohydrosilylation of **103** using chloroplatinic acid and a platinumdivinyltetramethyldisiloxane complex as the catalyst precursor gave at room temperature roughly equal amounts of **104** and **105** in more than 70% combined isolated yield [294].

Bifunctional crosslinking agents containing Si–H bond were synthesized by platinum-catalyzed selective hydrosilylation of $(CH_2{=}CHCH_2)_2Z$ ($Z = (CH_2)_4$, O-*p*-$C_6H_4CMe_2$-*p*-$C_6H_4O$, $O_2C$-*m*-$C_6H_4CO_2$, or $O_2CO(C_2H_4O)_2CO_2$) with 2,4,6,8-tetramethylcyclotetrasiloxane [295].

The $H_2PtCl_6$-catalyzed hydrosilylation of vinylferrocene by $H_8Si_8O_{12}$ gave the first organometallic monosubstituted octasilasesquioxane $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4CH_2CH_2)]H_7Si_8O_{12}$ [296]. A polysiloxane-supported sulfide-amine-platinum complex was found to be an effective catalyst for the hydrosilylation of olefins with triethoxysilane [297]. A silica-bound dithia-aza crown ether platinum complex



**102**



**103** **104** **105**

was found to be an efficient catalyst for the hydrosilylation of olefins with triethoxysilane [298].

Acrylate esters were selectively hydrosilylated with trichlorosilane or methyldichlorosilane in the presence of copper salts and tetramethylethylenediamine (TMEDA) [299]. E.g.:

$$Cl_3SiH + H_2C{=}CH\text{-}COOMe \xrightarrow[\text{TMEDA}]{\Delta,\ \text{CuCl}} Cl_3SiCH_2CH_2COOMe$$

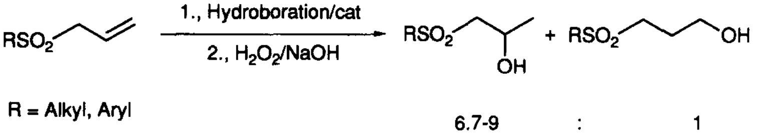
>95% yield

See also Ref. [122].

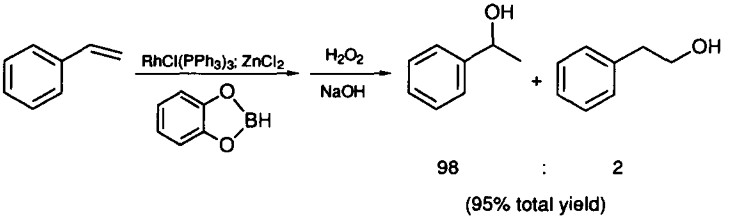
### 3.13. Hydroboration

A range of samarium(III) as well as other lanthanide complexes were found to catalyze the hydroboration of a broad selection of olefins with catecholborane [300]. Bis(mesityl)niobium was found to promote hydroboration of alkenes by catecholborane [301]. Hydroboration of alkenes by borohydride anion in the presence of $Cp^*_2TiCl_2$ was studied [302]. The complexes $RuCl_2(PPh_3)_4$, $RuCl_3(PPh_3)_2(MeOH)$, $RuHCl(PPh_3)_3$, $RuH_4(PPh_3)_3$, and $RuHCl(DIOP)_2$ were found to be catalysts for addition of catecholborane and 3-methyl-1,3,2-oxazaborolane to unhindered alkenes and alkynes [303].

Reaction of allyl sulfones with catecholborane catalyzed by $RhCl(PPh_3)_3$ was found to provide the Markownikoff product with high regioselectivity [304].



Various amounts of $BH_3$-derived products arising from rhodium-mediated catecholborane degradation were found in the rhodium-catalyzed hydroboration of 4-vinylanisole with catecholborane. The only catalyst precursors examined which did not lead to degradation of catecholborane were rhodium(I) chloride complexes containing basic monodentate phosphines [305]. Rhodium(I)-catalyzed hydroboration was the topic of a thesis [306]. The reversed regiochemistry of the rhodium-catalyzed hydroboration of styrenes by catecholborane could be further reinforced by the addition of some metal halides, Lewis acids and molecular sieves [307]. E.g.:



The addition of catecholborane to vinylarenes in the presence of $RhCl(PPh_3)_3$ was found to give Markownikoff hydroboration products exclusively, whereas the corresponding reaction with α-substituted vinylarenes gives good yields of vinylboronate ester resulting from dehydrogenative borylation [308].

Hydroboration of **106** with catecholborane in the presence of catalytic amounts of bis(chlorodicyclooctadienylrhodium)triphenylphosphine in THF followed by oxidative workup and acetylation gave **107** and **108** in 72% yield in a 30:70 regioisomer ratio [309].

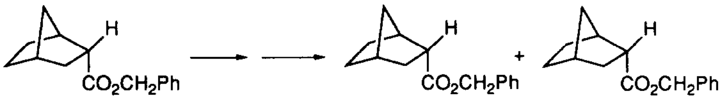
1-Arylethanols were prepared in up to 99% chemoselectivity and 94% ee from vinylarenes through asymmetric hydroboration with catecholborane catalyzed by a rhodium complex of **109** and oxidation with $H_2O_2$ [310].

Hydroboration of 1-(ethylthio-1-propyne (**110**) with catecholborane in the presence of 3 mol% $NiCl_2$(dppe) or $NiCl_2$(dppp) (dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane) gave excellent yields of **111** at room temperature [311].

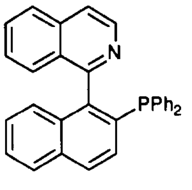
Optically active allenylboranes **113** were obtained by the palladium-catalyzed hydroboration of **112** using (*S*)-(−)-MeO-MOP (**114**) as a chiral phosphine ligand [312].

### 3.14. Hydroamination

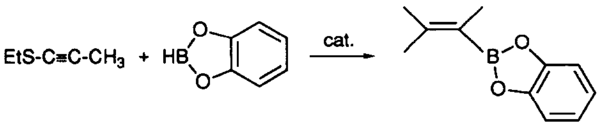
The kinetic and mechanism, and the diastereoselectivity of the organolanthanide-catalyzed hydroamination were studied in the case of the cyclization of *N*-unprotected amino olefins [313]. The regiochemistry of the stoichiometric and catalytic hydro-



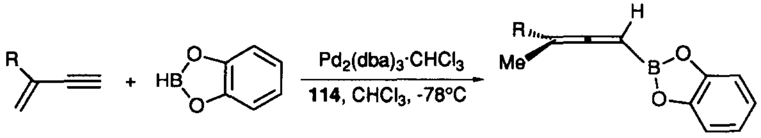
**106** **107** **108**



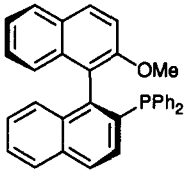
**109**



**110** **111**



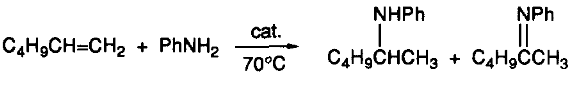
**112** **113**



**114**

amination of disubstituted alkynes by imidoziconium complexes was investigated [314].

A catalyst genarated from lithium anilide and $[(Et_3P)_2RhCl]_2$ was found to catalyze the regioselective hydroamination and dehydrogenative hydroamination of styrene or 1-hexene with aniline [315]. E.g.:

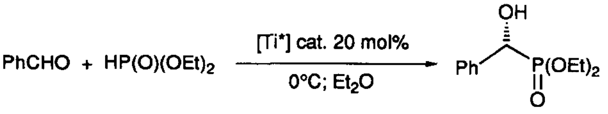


$$C_4H_9CH{=}CH_2 + PhNH_2 \xrightarrow[70^\circ C]{cat.} C_4H_9\overset{NHPh}{\overset{|}{C}}HCH_3 + C_4H_9\overset{NPh}{\overset{\|}{C}}CH_3$$

15 : 85

### 3.15. Hydrophosphonylation

A chiral titanium alkoxide derived from L-tartrate and $Ti(O^iPr)_4$ was found to be an effective catalyst for hydrophosphonylation of aldehydes and induce modest enantioselectivity in the reaction [316]. E.g.:



75% yield, 53% ee

The hydrophosphonylation of *p*-anisaldehyde using a chiral lanthanum binaphthol complex, prepared from $LaCl_3 \cdot 7H_2O$ and dilithium (*R*)-binaphthoxide, as the catalyst in THF at −40 °C resulted in 95% yield and 82% ee of the corresponding (*S*)-(−)-α-hydroxyphosphonates [317].

## 4. Oxidation

### 4.1. Catalytic oxidation of hydrocarbons and hydrocarbon groups with $O_2$

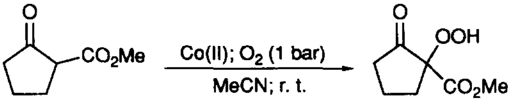
#### 4.1.1. Oxidation of saturated hydrocarbons

The partial oxidation of cyclohexane to cyclohexanol and cyclohexanone with dioxygen (1 bar) was affected by using samarium(III) chloride dissolved in a mixed solvent of acetic acid, methylene chloride and water in the presence of zinc powder at 40 °C [318]. Adamantane, ethylbenzene, and cyclohexane were catalytically and selectively oxidized to the corresponding alcohols and ketones with dioxygen (1.3 bar) at 82 °C using $[PW_9O_{37}\{Fe_2Ni(OAc)_3\}]^{10-}$ heteropolyanion as the catalyst [319].

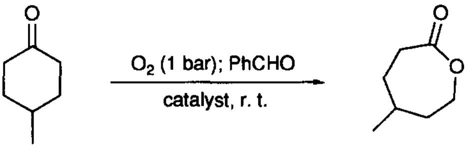
Poly(siloxane)-supported tetra(4-pyridyl)porphyrinatomanganese(III) was used as the catalyst for the oxidation of cyclohexene to cyclohe-2-en-1-one in methylene chloride, toluene or toluene/2-methyltetrahydrofuran at 30 °C in the presence of $NaBH_4$ under air oxygen. Turnovers up to 14000 were reported for the selective cyclohexanone formation [320].

The oxidation of alkenes by dioxygen in the trifluoroacetic acid solution in the presence of some ruthenium(III) $\beta$-ketoenolates was investigated. Heptane afforded a mixture of 1-, 2-, 3-, and 4-heptyl trifluoroacetate with 1, 31, 44, and 24% product distribution, respectively [321].

Unfunctionalized alkenes such as 1-dodecene, *trans*-stilbene, *cis*-2-octene, cholesteryl acetate, and linalool acetate were transformed into the corresponding epoxide by cobalt(II)-catalyzed in situ generated hydroperoxide from methyl-2-oxocyclopentane carboxylate and molecular oxygen [322].

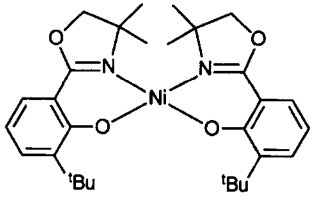


The influence of metal salts as catalysts in the Baeyer–Villiger oxidation of ketones to lactones by dioxygen in the presence of benzaldehyde was investigated. Copper(II)-acetate and nickel(oxa)$_2$ (**115**) were found to give the highest yields of lactone. E.g.:



94% yield

The copper complex of a polymeric porphyrin (tetrakis(*p*-hydroxyphenyl)porphyrin linked by *m*-benzene-disulfonate to form two-dimensional arrangements) was found to exhibit catalytic activity in oxidation of ethyl benzene to a mixture of $\alpha$-phenyl ethanol and acetophenone, and cyclohexene and isobutyl alcohol by dioxygen (1 bar) without any solvent [324]. 2,4,6-Trimethylphenol was selectively oxidized to 3,5-dimethyl-4-hydroxybenzaldehyde by molecular oxygen in the presence of a



**115**

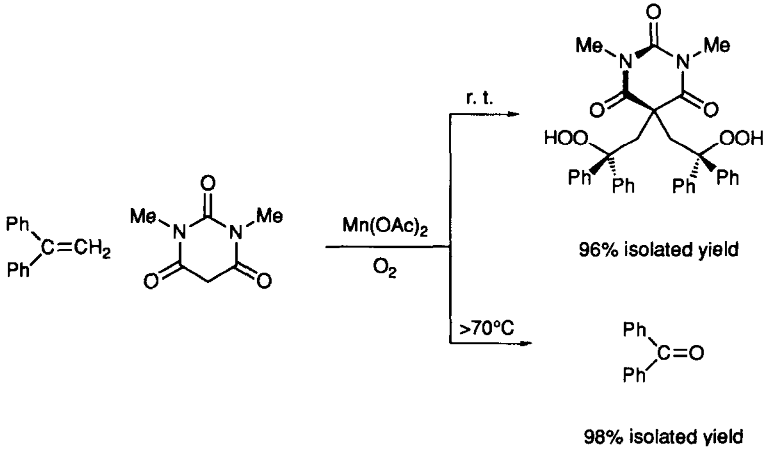
copper(II) chloride-oxime catalyst in alcohol at 40–60 °C and atmospheric pressure [325].

The selective oxidation of cyclohexane to cyclohexanol and cyclohexanone by molecular oxygen was studied using various metalloporphyrins in the presence of ascorbic acid. The effects of the central metal ion, the axial ligand, the ratio of substrate to catalyst, and pH on the reaction were investigated [326]. See also Refs. [348,372,412].

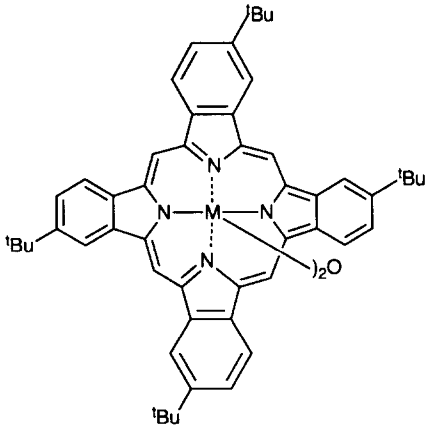
### 4.1.2. *Oxidation of olefins*

Cobalt chloride in diglyme was found to be a useful catalyst for the allylic oxidation of cyclohexene by dioxygen, affording 2-cyclohexen-1-ol as the major product and 2-cyclohexen-1-one as the by-product. In the presence of *N*-methylpyrrolidone or by using vanadium compounds as the catalyst, 2-cyclohexen-1-one is the major product [327].

The reactions of 1,1-disubstituted ethenes with barbituric acid and its derivatives in the presence of manganese(II) acetate and air were found to yield 5,5-bis (2-hydroperoxyalkyl)barbituric acids in 62–99% yields at room temperature. The reaction at 70 °C yields the corresponding benzophenones [328]. E.g.:



Soluble iron(III) and manganese(III) phthalocyanines **116** and **117** were tested in oxygenation of various alkenes such as 1-hexene, cyclohexene, *cis*, *trans*-cycloocta-1,5-diene, dicyclopentadiene, and α-pinene at room temperature [329].



**116** M = Fe

**117** M = Mn

Susceptibilities of different molecular species of purified soybean oil triglycerides were compared in both non-catalyzed and iron(II)-catalyzed oxidation systems at 37 °C. In both systems, with some exceptions, epoxidation rates increased as the number of double bonds in the fatty acyl chains increased, for molecular species having the same total carbon number. In the case of triglycerides having the same number of double bonds, the oxidation rate was inversely proportional to the number of carbon atoms in the fatty acyl chain [330].

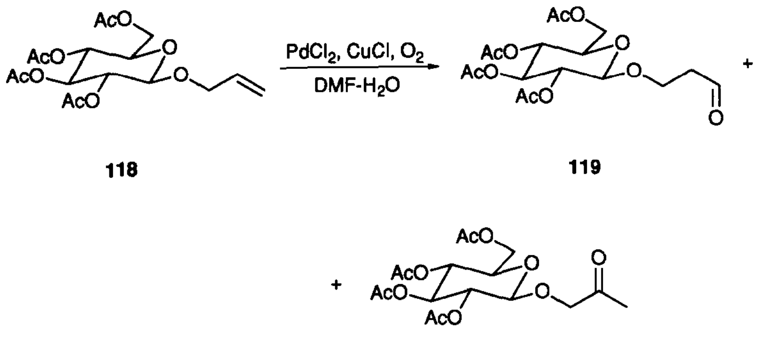
The cobalt-catalyzed oxidation of activated hydrocarbons under an atmosphere of dioxygen was investigated [331]. The selective catalytic oxygenation of styrene to a mixture of acetophenone and 1-phenyl-ethanol at 60 °C was investigated using various cobalt Schiff base complexes as the catalyst. The rate of the reaction was found to depend on the shape but not on the redox potential $E^\circ(Co^{II}/Co^{III})$ of the complex catalyst [332]. Various aromatic olefins and acrylic acid derivatives were converted to benzyl alcohols and α-hydroxyalkanoic acid derivatives in good yields by the reductive oxygenation with dioxygen and triethylsilane in the presence of a catalytic amount of [5,10,15,20-tetrakis(2,6-dichlorophenyl)porphinato]cobalt(II) as the catalyst, followed by treating the reaction mixture with trimethyl phosphite at room temperature [333].

The Wacker oxidation of **118** resulted in a mixture of **117** and **120** in essentially quantitative yield [334].

The allylic acetoxylation of cyclohexene by 5 mol% palladium acetate and 5 mol% iron(III) nitrate in acetic acid under an atmosphere of dioxygen gave cyclohexenyl acetate in 92% yield [335]. See also Ref. [324].

### *4.1.3. Epoxidation of olefins*

$NPV_6Mo_6$-type mixed heteropolyoxometalate was found to epoxidize olefins with dioxygen in the presence of 2 equiv of 2-methylpropanal at 25 °C and 1 bar. In the absence of olefins, the aldehyde is efficiently converted to the corresponding carboxylic acid [336]. The $PW_{11}CoO_{39}^{5-}$-catalyzed epoxidation of cyclohexene, 1-decene, styrene [337] (*R*)-(+)-limonene, 4-vinyl-1-cyclohexene, and 1-methyl-1,4-cyclohexadiene [338] by molecular oxygen in the presence of aldehydes was studied.



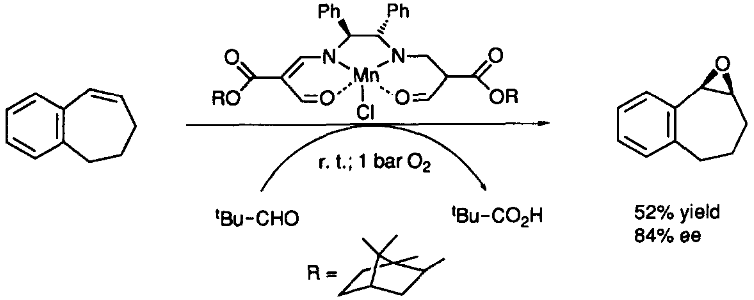
**118**

**119**

**120**

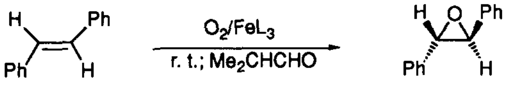
The catalytic epoxidation of styrene by dioxygen in the presence of *m*-oxo mixed-metal acetate complexes Fe$_2^{III}$Zn$^{II}$, Co$_2^{III}$Co$^{II}$, and Cr$_2^{III}$Fe$^{II}$ was carried out in the absence of solvent [339].

The asymmetric aerobic epoxidation of unfunctionalized olefins was found to be catalyzed by optically active α-alkoxycarbonyl-β-ketoiminato manganese(III) complexes [340]. E.g.:

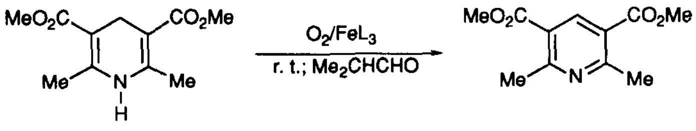


52% yield
84% ee

The synthetic metalloporphyrin analogue FeL$_3$ (**121**) was found to catalyze the epoxidation of olefins and the dehydrogenation of 1,4-dihydropyridines by dioxygen (1 bar) at room temperature in the presence of isobutyraldehyde [341]. E.g.:



96% yield



100% yield

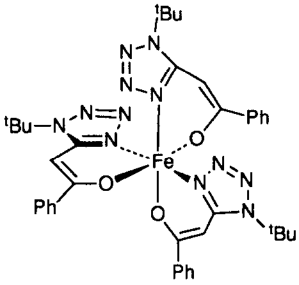
Epoxidation of 2-norbornene with molecular oxygen (10 bar) was achieved by utilization of $FeCl_2$ or $Co(OAc)_2$ and the *N*-heterocyclic podand ligand **122** at 70 °C without the need for a coreductant [342].

Various trisubstituted olefins were smoothly monooxygenated into the corresponding epoxides in high yields under neutral conditions by the combined use of molecular oxygen and propionaldehyde diethyl acetal in the presence of bis(3-methyl-2,4-pentadionato)cobalt(II) as the catalyst [343].

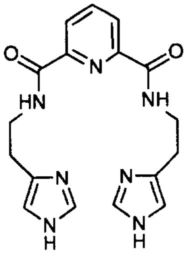
Nickel(II) complexes (**123**, **124**, and **125**) were tested as the catalysts in the epoxidation of stilbene with 1 bar dioxygen in the presence of an aldehyde. No asymmetric induction from catalyst **123** and **124** was observed and the substitution in **125** gave no remarkable difference on the rate of epoxidation [344].

Selective epoxidation of various olefins by compressed air (10 bar) were accomplished using clay-impregnated nickel acetylacetonate catalyst and isobutyraldehyde as co-oxidant in methylene chloride solution at room temperature [345]. The structure-activity relation of aliphatic and aromatic aldehydes to serve as a sacrificial auxiliary in the above epoxidations has been investigated [346]. The preparation of a catalyst by impregnating montmorillonite with nickel acetylacetonate and its application for epoxidation of linear and cyclic alkenes was described [347].

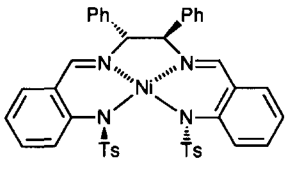
Oxidation of alkanes to the corresponding alcohols and ketones and epoxidation



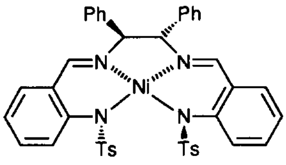
**121**



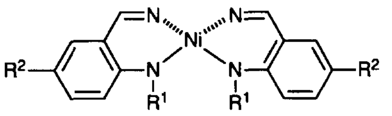
**122**



**123**



**124**



**125**

$R^1$ = H, Cl, Me;

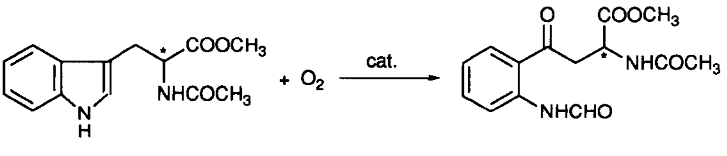
$R^2$ = Ts, $CF_3SO_2$, $4\text{-}MeOC_6H_4SO_2$
Bz, $PhCH_2$

of alkenes were performed at room temperature with molecular oxygen (1 bar) in the presence of an aldehyde and a copper salt catalyst such as $Cu(OH)_2$ [348]. Copper(I) or copper(II) salt–ascorbic acid systems were found to catalyze the facile epoxidation of *trans*-stylbene without concomitant formation of benzaldehyde, by utilizing molecular oxygen under mild conditions [349]. See also Refs. [322,329].

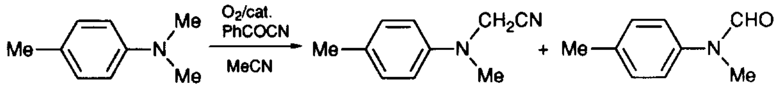
### 4.1.4. Oxidation of aromatics

The oxidation of isopropylbenzene to acetophenone and methanol by dioxygen catalyzed by steroid-metalloporphyrins (steroid = estradiol, estrone, ethynylestradiol; metal = $Co^{2+}$, $Zn^{2+}$, $Mn^{2+}$, $Fe^{2+}$) was studied [350].

The catalytic efficiency of poly(ethylene glycol)-modified and bovine serum albumin-bonded tetra(*p*-carboxyphenyl)-porphyrin manganese(III) chloride for stereoselective tryptophan 2,3-dioxygenase-like reaction in organic/aqueous solvents was reported [351].



Selective oxidation of ethylbenzene, propylbenzene, and butylbenzene under 1 bar diogygen or air at 105 °C in the presence of ruthenium–polymer-bound 2,2′-bipyridine complexes affords the corresponding ketone and alcohol in good yield [352]. The dioxygenolysis of 3-methylindole catalyzed by a series of electronically and sterically designed cobalt(II) Schiff base complexes was found to give 2-(*N*-formylamino)acetophenone as the sole product at 25 °C [353].



**126** **127** **128**

### 4.1.5. Miscellaneous oxidations

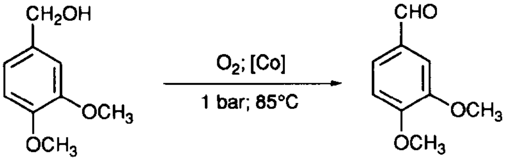
The oxidation of **126** with molecular oxygen in the presence of benzoyl cyanide and a catalyst gave a mixture of **127** and **128**. In the case of iron(III) chloride as the catalyst, **127** was obtained in 60% isolated yield. Cobalt(II) chloride was found to be a less selective catalyst. Manganese(II) chloride or copper(I) chloride led mainly to **128** in 53% and in 77% yield, respectively [354].

## 4.2. Catalytic oxidation of o-containing organic compounds with $O_2$

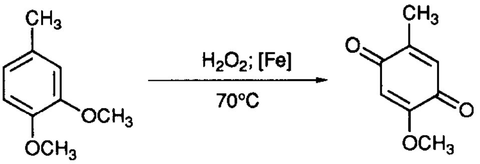
### 4.2.1. Oxidation of alcohols

The catalytic properties of $MnMoO_4$-based catalysts for methanol air-oxidation to formaldehyde were studied. The effect of temperature, flow rate, and gas mixture composition on the catalytic activity was established [355].

Water-soluble metallophthalocyanines and metalloporphyrins were tested as catalysts for the aqueous oxidations of lignin model compounds with dioxygen and with hydrogen peroxide. Cobalt and iron phthalocyaninetetra(sodium sulfonate) were found to be the most active catalyst using $O_2$ and $H_2O_2$ as oxidant, respectively [356]. E.g.:

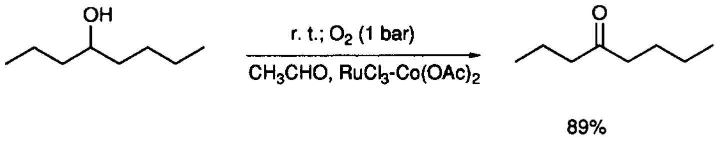


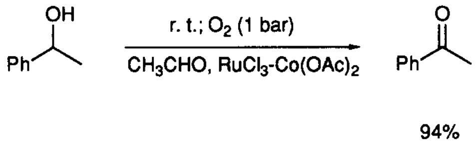
100% yield

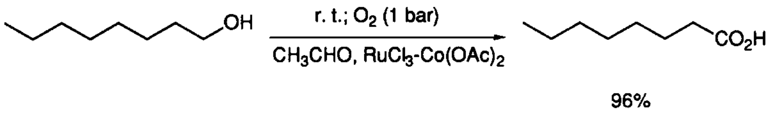


4% yield

Oxidation of secondary and primary alcohols at room temperature with molecular oxygen (1 bar) to the corresponding ketone and carboxylic acid, respectively, were efficiently performed (78–98% isolated yields) in the presence of an aldehyde and $RuCl_3$–$Co(OAc)_2$ bimetallic catalyst [357]. E.g.:







Efficient catalytic dehydrogenation of $Ph_2CHOH$ by 2,2′-bipyridine-copper(I) chloride–dioxygen system in acetonitrile has been reported [358]. See also Ref. [324].

### 4.2.2. *Oxidation of phenols*

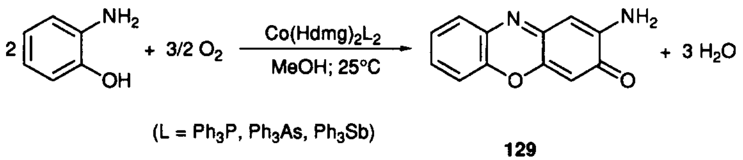
Aerobic oxidation of hydroquinone to 1,4-benzoquinone was used as a simple test for determining the catalytic activity of iron phthalocyanine from various sources. The catalytic activity was found to be dependent not only on the nature and origin of the catalyst but also on the content of the solvent [359].

The rate of autoxidation of catechols in copper(II) micelle solutions was studied at 25 °C in the acidic pH region [360]. Molecular recognition in the oxidation of catechols by dicobalt-1,4,7,13,16,19-hexaza-10,22-dioxacyclotetracosane dioxygen complexes was observed. Thus, 4-methylcatechol gave 3-methyl-*cis*, *cis*-muconic acid, but 3,5-dibutylcatechol in place of 4-methylcatechol remained unchanged [361]. Cobaloxime(II) derivatives catalyze the oxidation of 2-aminophenol to **129** by $O_2$ at atmospheric pressure [362].

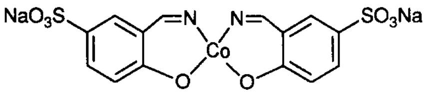
The water-soluble cobalt(II) complex **130** was found to be an effective catalyst in the autoxidation of 2,6-di-*tert*-butylphenol in aqueous medium at 40 °C [363].

The kinetics of oxidation of hydroquinone catalyzed by a cobalt complex with 2,2′-bipyridyl fixed to silica were studied [364].

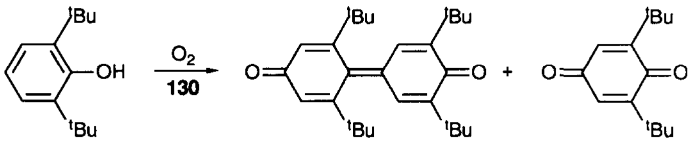
The copper(I) dioxygen complex of **131** was found to be a catalyst for the oxidation



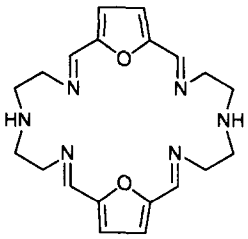
**129**



**130**



85 15



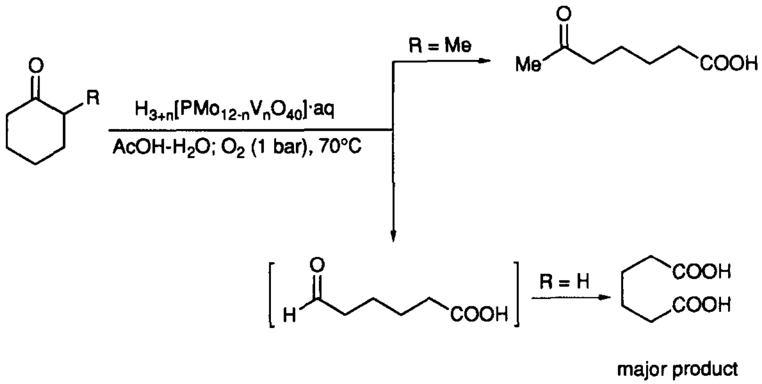
**131**

of hydroquinones to the corresponding benzoquinones, ascorbic acid to dehydroascorbic acid, and phenols to their 1,4-benzoquinones and diphenoquinones, in the presence of excess dioxygen [365].

A rate study of the copper-catalyzed autoxidation of 3,5-di-*tert*-butylcatechol has shown that there is a dramatic enhancement of the rate of oxidation when the medium is changed from the metal ion solution to a micellar solution at 25 °C and pH = 5.7 [366]. The catalytic oxygenation of hydroquinone to quinone using Schiff base complexes of copper(II) derived from 2-phenyl-1,2,3-triazole-4-carboxaldehyde and aniline was investigated [367]. Dinuclear copper(II) complexes of differing magnetic and redox properties were investigated for their catalytic activity in the oxidation of 3,5-di-*tert*-butylcatechol and ascorbic acid by dioxygen [368].

### *4.2.3. Oxidation of aldehydes and ketones*

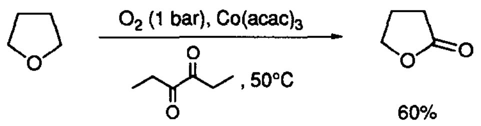
Oxidation of 2-methylcyclohexanone and cyclohexanone by dioxygen catalyzed by vanadium-containing heteropolyanions gave 6-oxoheptanoic acid and adipic acid, respectively [369].



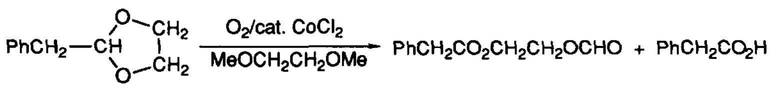
See also Refs. [336,365].

### 4.2.4. *Miscellaneous oxidations*

In the presence of a catalytic amount of tris(acetylacetonato)cobalt(III), tetrahydrofurans were found to be oxygenated into the corresponding $\gamma$-butyrolactones with dioxygen (1 bar) at 50 °C in the presence of an $\alpha$-diketone having hydrogen atom next to the carbonyl carbon [370]. E.g.:



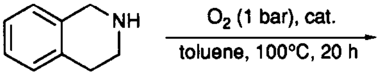
The cobalt(II)-catalyzed oxidation of 2-substituted 1,3-dioxolanes with molecular oxygen was found to afford formate ester and acids [371]. E.g.:



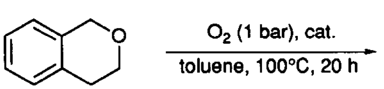
See also Ref. [372].

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

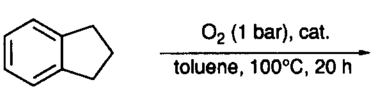
Mixed addenda heteropolyoxometalate, $NPV_6Mo_6$, prepared from $Na_2MoO_4\cdot 2H_2O$, $NaVO_3$, $H_3PO_4$, and $NH_4Cl$, was found to be an efficient catalyst in toluene solution at 100 °C for the oxidative dehydrogenation of a variety of benzylic amines to the corresponding Schiff-base imines and for the selective oxidation of isochromon and indan to 3,4-dihydroisocoumarin and 1-indanone, respectively, with dioxygen [372].



82% conversion
>99% selectivity

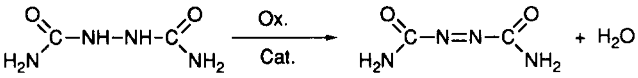


86% conversion
88% selectivity



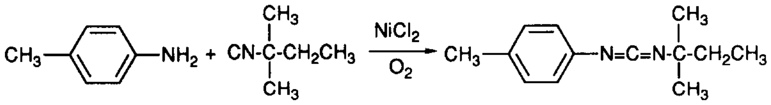
74% conversion
64% selectivity

Heteropolyacids, such as $H_9PV_6Mo_6O_{40}$, were found to catalyze the oxidation of hydrodicarboxamide to azodicarboxamide by dioxygen at 50 °C and 1 bar in the presence of sulfuric acid [373].

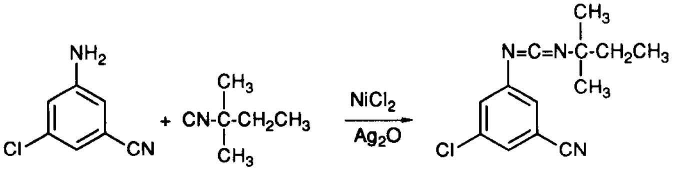


The homogeneous catalytic oxidation of hydrazobenzene by dioxygen in methanol was investigated using tetradentate Schiff-base cobalt(II) complexes such as Co(II)(SED)$(py)_2$ (SED = *N*,*N*′-ethylenebis(salicylideneiminato)) as the catalysts. The major product of hydrazobenzene oxidation by superoxo-type catalyst was found to be *trans*-azobenzene, whereas *cis*-azobenzene was obtained as a major product with a μ-peroxo-type catalyst. The kinetics of the oxidation reactions were studied [374].

Nickel(III)-promoted DNA cleavage with ambient dioxygen has been communicated [375]. Unsymmetrical carbodiimides were prepared in up to 88% yield by the nickel(II)-catalyzed oxidation of isocyanides and primary amines using molecular oxygen as an oxidant. Also good yields were obtained by using $Ag_2O$ or HgO as an oxidant [376]. E.g.:



88% isolated yield



86% isolated yield

The copper(I) chloride-catalyzed oxygenation of **132** by dioxygen in anhydrous acetonitrile leads to highly reactive intermediate **133** which provides **134** in the presence of dialkylamines in >50% yield [377]. See also Ref. [341].

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

Catalytic activities of $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, and $Cu^{2+}$ salts of $FeCl^{2+}$-, $Co^{2+}$-, $Ni^{2+}$, and $Cu^{2+}$-phthalocyaninetetracarboxylic acids in the autoxidation of thiophenol were examined. The iron(III) salt of cobalt phthalocyaninetetracarboxylic acid was found to have the highest activity [378].

Catalytic oxygenation of 2-mercaptoethanol at 25 °C and atmospheric pressure by charcoal-supported sterically hindered cobalt(II)-phthalocyanines was reported. High and durable activity of the catalyst was observed in the case of cobalt(II)-tetra-*tert*-butylphthalocyanine by following the reaction through 8000 cycles [379]. The catalytic properties of silica-attached cobalt phthalocyanines were studied in the dioxygen oxidation of cysteine to cystine [380]. The catalytic activities of different cobalt(II) phthalocyanines on silica in the oxidation of 2-mercaptoethanol by molecular oxygen were studied. Electron-withdrawing substituents increase and electron-donating substituents decrease the catalytic activity [381].

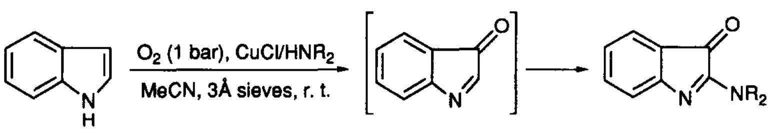
Triphenylphosphine was oxidized to triphenylphosphine oxide with molecular oxygen at room temperature under atmospheric pressure in the presence of $Pd(OAc)_2$ as the catalyst precursor [382].

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

#### 4.5.1. *Oxidation of hydrocarbons or hydrocarbon groups*

Thorium peroxo complexes such as $ThO_2$(anthranilic acid)$_2$ and $ThO_2$ (bis(salicylaldehyde)ethylenediamine) were used as catalysts for the oxidation of various olefins by *tert*-butylhydroperoxide [383].

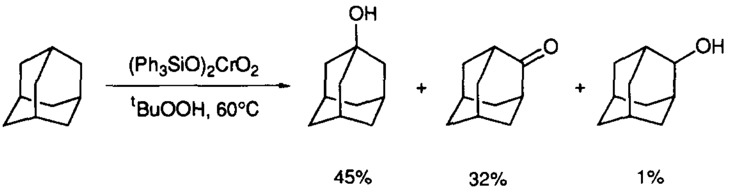
Benzene and substituted benzenes were hydroxylated at room temperature to the corresponding monophenols by hydrogen peroxide in MeCN in yields ranging from acceptable to fair using $VO(O_2)(PIC)(H_2O)_2$ (PIC) = picolinic acid) as the catalyst [384]. Cyclohexane and other alkanes, and benzene were oxidized with hydrogen peroxide in acetonitrile at 20–70 °C in the presence of the catalyst $Bu_4NVO_3$-pyrazine-2-carboxylic acid to afford, after reduction with $PPh_3$ the corresponding alcohol and carbonyl derivatives, and phenol, respectively [385]. Enhanced stability of the active centers, compared with homogeneous vanadyl acetylaacetonate, was



**132** **133** **134**

observed in the liquid-phase oxidation of anthracene with hydrogen peroxide in the presence of heterogenized vanadyl acetylacetonate [386].

Among various chromium(VI) compounds $(Ph_3SiO)_2CrO_2$ was found to be the most effective catalyst for the oxidation of adamantane by commercial 70% aqueous *tert*-butyl hydroperoxide. Using 10 mol% catalyst for each mol of oxidant at 60 °C, 78% total yield of oxidation products were obtained [387].



Acetylene was oxidized to glyoxal by dilute hydrogen peroxide at 25 °C in the presence of Mo(VI) or W(VI) salts as catalysts and mercuric acetate as co-catalyst [388].

Manganese clusters, $[Mn_2O(OAc)(tmima)_2](ClO_4)_3$ (tmima = tris[(1-methylimidazol-2-yl)methyl]amine), $Mn_3O(OAc)_6(py)_3](ClO_4)$, $Mn_4O_2(OBz)_7(bipy)_2$, and $[Mn_4O_2(OBz)_7(bipy)_2](ClO_4)$ were found to functionalize ethane, propane, cyclohexane, adamantane, and toluene to their respective alcohols, aldehydes, and ketones with monooxygen transfer reagents, *tert*-butylhydroperoxide or iodosobenzene, in the presence of dioxygen [389]. The reaction of singlet oxygen with adamantylideneadamantane in the presence of iron(III) or manganese(III) porphyrin chloride was found to caused cooxidation of hydrocarbons, olefins and heteroatoms in substantial yields. The active oxidizing species is probably a high valency metal oxo species generated by an oxygen transfer from a perepoxide intermediate to the metal porphyrin chloride [390]. Kinetic isotope effects in alkane hydroxylations catalyzed by manganese and iron porphyrin complexes were studied with 1,3-dideuterioadamantane as substrate. The highest kinetic isotope effect values were obtained with Fe(TMP)Cl/NaOCl (TMP = *meso*-tetramesitylporphyrin) and Fe(TMP)Cl/PhIO: $8.71 \pm 0.20$ and $7.52 \pm 0.21$, respectively [391].

Adamantane and cyclohexane were effectively oxidized in benzene solution at 25 °C by *m*-chloroperbenzoic acid, to adamantanols and cyclohexanol, respectively, in the presence of an iron porphyrin ligated by an alkyl thiolate anion in axial position [392].

The ($\mu$-oxo)diferric complex $[Fe_2(TPA)_2O(OAc)](ClO_4)_3$ (TPA = tris(2-pyridylmethyl)amine was found to be an efficient catalyst for cyclohexane oxidation with *tert*-butyl hydroperoxide, affording cyclohexanol, cyclohexanone, and (*tert*-butylperoxy)cyclohexane at ambient temperature and pressure under an argon atmosphere [393].

The oxidation of olefins by iodosobenzene in the presence of various iron(III) complexes was studied. Cyclohexene was oxidized at room temperature to a mixture of cyclohexene oxide, cyclohexenol, and cyclohexenone. The effect of added surfactants was studied [394].

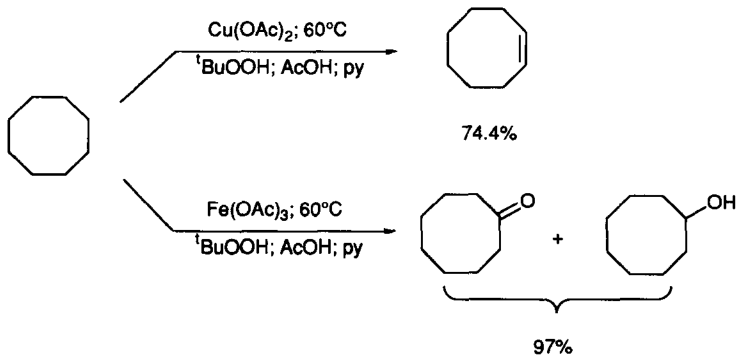
Four indolic alkaloids, β-carboline, reserpine, ajmaline, and ibogaine were oxidized in a Gif system leading to alicyclic hydroxylation of the starting materials [395].

Cycloalkanes were transformed into monosubstituted cycloalkyl derivatives (chloride, azide, cyanide, thiocyanate, dicycloalkyl disulfide, or nitroalkane) in mostly good efficiencies (up to 70%) by treatment with *tert*-butyl hydroperoxide in pyridine/acetic acid containing $Fe(NO_3)_3 \cdot 9H_2O$, in the presence of alkali metal salts (LiCl, $NaN_3$, $[Et_4N]CN$, NaSCN, $Na_2S$ or $NaNO_2$, respectively [396]. The effect of triphenylphosphine in the $GoAgg^{II}$ system [$FeCl_3 \cdot 6H_2O$ (cat.), $H_2O_2$ in pyridine-acetic acid] was investigated. It was found that by addition of $PPh_3$ and alkali metal salts LiCl, NaSCN, or $NaN_3$ the usual formation of ketone and alcohol was replaced by the formation of chloro-, rhodanato-, or azidoalkene [397]. The nature of the iron(III) species present in solution before the addition of hydrogen peroxide in the oxidation reaction of saturated hydrocarbons by hydrogen peroxide in pyridine-acetic acid solution in the presence of picolinic acid ($GoAgg^{III}$ system) was investigated. The results indicate that the $GoAgg^{III}$ system is a model that mimics single-iron non-heme enzymic oxidations [398].

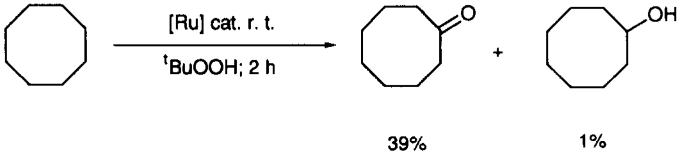
The addition of alkali was found to strongly accelerate the oxidation of cyclohexane by an iron tetramesitylporphirin-NaOCl system [399]. The oxidation of cyclohexane to cyclohexanol by sodium hypochlorite in the presence of iron(III) tetramesitylporphyrin as the catalyst was studied. At low concentrations of sodium hydroxide the oxidation proceeds selectively with an isotope effect ($k_H/k_D$) of 21.9. At higher concentrations of sodium hydroxide the oxidation rate increases by a factor of ~10, the selectivity is changed, and the isotope effect decreases to 11.2 [400].

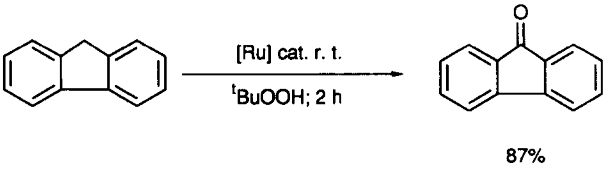
To illustrate biomimetic systems, the oxidation of ethylbenzene to acetophenone with hydrogen peroxide, catalyzed by iron(III), at room temperature was described as a teaching experiment [401].

Cycloalkanes were transformed into the corresponding cycloalkenes or into a mixture of ketone and alcohol in Gif-type reactions in the presence of catalytic amounts of $Cu(OAc)_2 \cdot H_2O$ or $Fe(OAc)_3$, respectively [402]. E.g.:



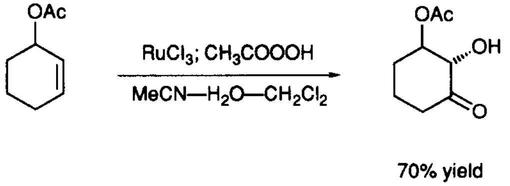
A ruthenium(III) analogue of the Gif-system, $RuCl_3$/acetic acid/pyridine/$KHSO_5$, was found to oxidize cyclohexane to cyclohexanone selectively at room temperature. This system yields 2.8% cyclohexanone based on $KHSO_5$ [403]. Linear and cyclic alkanes were converted efficiently into the corresponding ketones along with a small amount of alcohols at room temperature with *tert*-butyl hydroperoxide in the presence of $RuCl_2(PPh_3)_2$ as the catalyst. Kinetic study revealed that the reaction involves hydrogen atom abstraction from the alkane by oxoruthenium(IV) species [404]. E.g.:





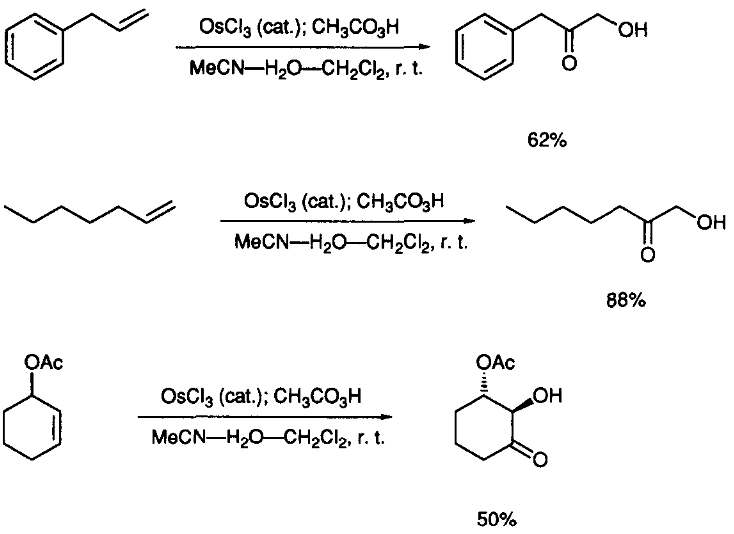
Hydroxylation and/or ketonization of adamantane, cyclooctane, and hexane was achieved by using iodosobenzene or aqueous mono-persulfate at room temperature in the presence of catalytic amounts of ruthenium(III)-diphosphino complexes dissolved in dichloromethane [405].

The reaction of alkenes with peracetic acid at room temperature in the presence of ruthenium(III) chloride as the catalyst gave the corresponding α-ketols [406]. E.g.:

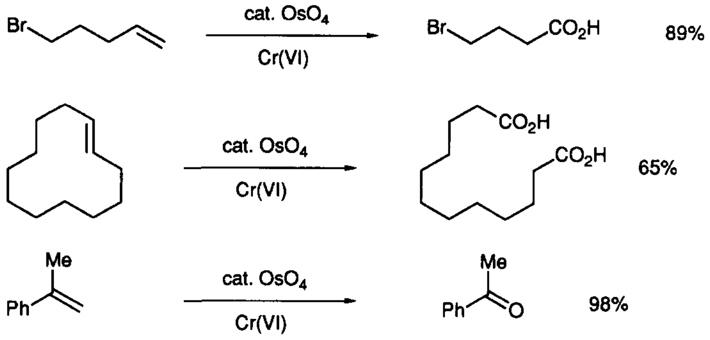


The ruthenium-catalyzed oxidative cleavage of olefins with terminal and internal double bonds by peracetic acid and hydrogen peroxide was studied [407]. Ethylbenzene and a number of substituted benzene derivatives such as benzyl alcohol, benzaldehyde, benzoic acid, benzonitrile, benzyl chloride and benzyl bromide was found to be oxidized at the benzene ring to carbon dioxide and water when reacting at room temperature with aqueous persulfate in the presence of catalytic amounts of ruthenium or osmium complexes [408].

Osmium trichloride in a two-phase aqueous system was found to be a catalyst for the oxidative transformation of alkenes to α-ketols with peracetic acid at room temperature [409]. E.g.:



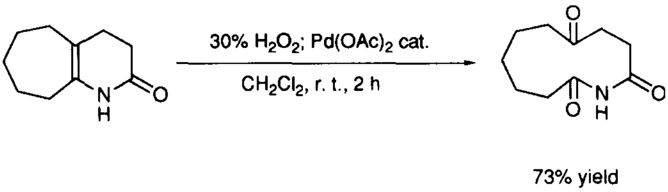
A combination of a catalytic amount of $OsO_4$ and stoichiometric chromate (Jones reagent) in acetone was found to oxidize various type of alkane into acids and/or ketones at room temperature [410]. E.g.:



The role of alkylperoxo complexes of cobalt(III) in catalytic oxidation of cyclohexane by cumene hydroperoxide in the presence of bis(acetyl-acetonato)cobalt(II) was investigated by $^1H$ and $^{59}Co$ NMR studies. It was concluded that the role of the cobalt catalyst consists in the generation of alkylperoxo and alkoxy radicals [411].

Bis(pyridine)copper(I) was found to activate hydrogen peroxide and *tert*-butyl hydroperoxyde for the selective ketonization of methylenic carbon of cyclohexane or ethylbenzene at 24 °C under argon. In the presence of dioxygen (1 bar) higher conversion efficiencies were observed. Bis(bipyridine)cobalt(II) complex in combination with *tert*-butyl hydroperoxide also activates dioxygen for ketonization of methylenic carbons but is about one-half as efficient as the $Cu^I(bpy)_2^+/{}^tBuOOH$ combination [412].

Terminal olefins were oxidized by hydrogen peroxide under mild conditions in excellent yields and selectivities to methyl ketones in the presence of tetrakis(triphenylphosphine)palladium(0) as the catalyst [413]. Oxidative cleavage of various ene-lactams by hydrogen peroxide at room temperature in the presence of palladium(II) acetate as the catalyst gave the corresponding macrocyclic ketoimides [414]. E.g.:



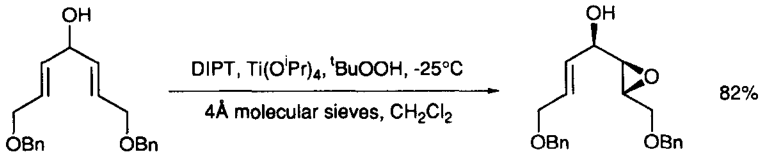
A catalyst comprising $(MeCN)_2PdCl_2$, CuCl and LiCl or NaCl in *tert*-butanol gave unusually high selectivities to aldehydes in oxygenation of terminal olefins. Thus, at 60 °C and 3 bar dioxygen allyl acetate gave 60% combined yield with 75% aldehyde selectivity [415]. The mixed catalyst $Pd(OAc)_2$–$Cu(OAc)_2$ was found to promote the carboxylation of propane [416] and cyclohexane [417] with CO and $K_2S_2O_8$ in higher yield than either a Pd(II) or Cu(II) catalyst alone at 80 °C, $P_{CO}$ = 20 bar, in trifluoroacetic acid. In the best cases up to 10% yield of the corresponding carboxylic acids were obtained in 20 h. The carboxylation of *p*-xylene with the mixed-metal catalyst under the above conditions gave 2,5-dimethylbenzoic acid. See also Refs. [430,437,438,464,558].

### *4.5.2. Epoxidation of olefins*

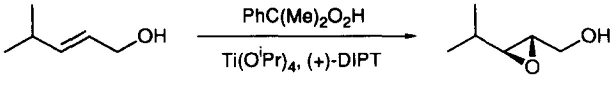
Scandium(III) porphyrin complex was found to show a high catalytic activity for styrene epoxidation under anaerobic conditions with *tert*-butyl hydroperoxide as the oxidant [418].

The Katsuki–Sharpless asymmetric epoxidation was applied in preparation of **136** from **135** [419].

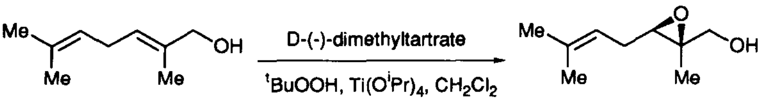
The Sharpless asymmetric epoxidation and dihydroxylation was applied in the synthesis of the higher dipteran juvenile hormone III bisepoxide from geraniol [420]. Asymmetric epoxidation of **137** was applied to prepare **138** in 82% yield [421].



**135** **136**



**137** **138**



**139** **140**

The epoxiation of **139** gave **140** in 90% yield and >95% ee [422].

The asymmetric epoxidation of **141** was reported [423].

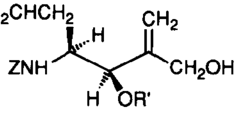
The Sharpless asymmetric epoxidation was applied in the case of alkenylsilanols, such as $PhCH{=}CHSiMe_2OH$, to obtain the corresponding chiral epoxysilanols [424]. The asymmetric epoxidation of **142** gave **143** in 94% yield and 97% ee [425].

The Sharpless asymmetric epoxidation of **144** gave **145** in 70% yield and 98% ee [426].

A convenient diastereoselective synthesis of epoxy diols in a two-step one-pot procedure was described. For example, the allylic alcohol **146** was converted diastereoselectively into the epoxy diols **147** by adding a catalytic amount of $Ti(O^iPr)_4$ to a photooxygenated solution of **146** [427].

The Sharpless asymmetric epoxidation of the alcohol **148** as part of the synthetic strategy for the preparation of perdeuterated deoxyribose and deoxyribonucleosides has been applied [428].

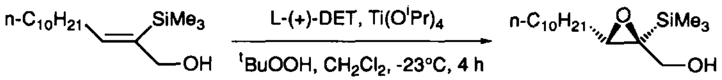
Epoxidation of olefins with *tert*-butyl hydroperoxide, as the oxidant, and vanadium pentoxide as the catalyst was studied [429]. Vanadium complexes formed from $VO(acac)_2$ in epoxidation of cyclohexene by organic hydroperoxides were characterized in situ with $^{51}V$ and $^1H$ NMR and EPR spectroscopy [430]. The effect of solvent, temperature, substituents and pH on the yield of epoxidation of various substituted chalcones with *tert*-butyl hydroperoxide using $Na_3[VO_2(EDTA)]$ as the



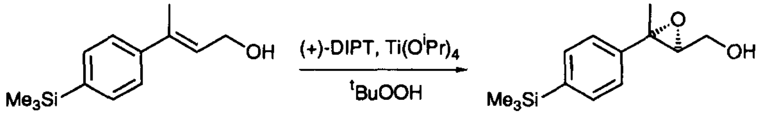
R' = (+)-PhC(OMe)(CF₃)CO

Z = benzyloxycarbonyl

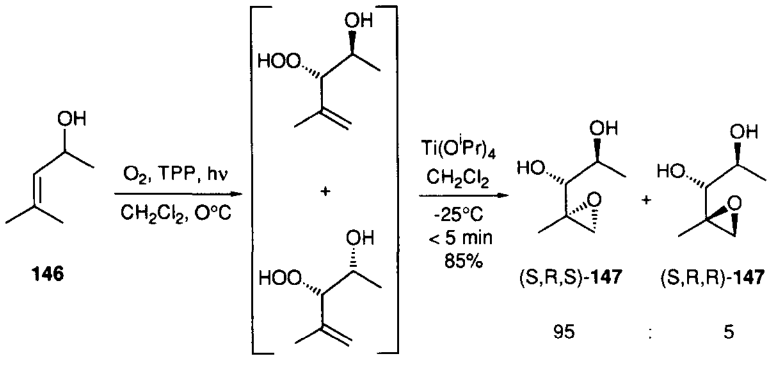
**141**

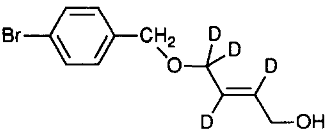


**142** **143**



**144** **145**



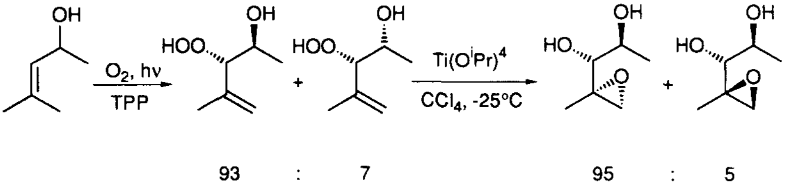


**148**

catalyst was studied [431]. (*Z*)-3-Methyl-3-penten-2-ol was used as stereochemical probe for 1,2 versus 1,3 allylic strain in epoxidation of chiral allylic alcohols with $VO(acac)_2/^tBuOOH$ [432]. The epoxidation of maleic, fumaric, and crotonic acids with hydrogen peroxide was studied using a resin-supported vanadium(IV) catalyst [433].

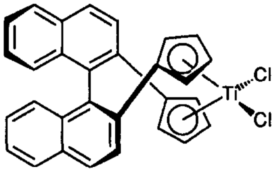
3,4,6-Tri-*O*-Benzyl-β-<SCP>D</SCP>-glucose was tested as chiral template for the epoxidation reaction of allylic ethers. The vanadium, molybdenum, or titanium-catalyzed epoxidation of *trans*-2′-butenyl 3,4,6-tri-*O*-benzyl β-D-glucopyranoside gave only 0–40% yield of the desired diastereomer epoxides [434].

In situ prepared hydroperoxy homoallylic alcohols obtained through the photooxygenation of chiral allylic alcohols were converted into epoxy diols under the catalytic action of $Ti(O^iPr)_4$ [435].



Asymmetric epoxidation of unfunctionalized alkenes (3-hexene, styrene, vinylcyclohexane, 2,5-dimethyl-3-hexene, 2,3-dimethyl-1-butene) with *tert*-butyl hydroperoxide in the presence of chiral titanocene dichloride complex **149** as a catalyst was examined at 80 °C. The best result (45 turnovers and 16% ee) was obtained with 3-hexene, a sterically unhindered *trans*-disubstituted alkene [436].

In situ characterization of the intermediate alkylperoxo complexes of Mo(VI),



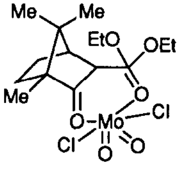
**149**

V(V), and Co(III) in the course of homogeneous epoxidation of cyclohexene and oxidation of cyclohexane from simultaneously recorded $^{95}Mo$, $^{51}V$ or $^{59}Co$ NMR spectra and $^{1}H$, $^{17}O$ NMR spectra was presented [437].

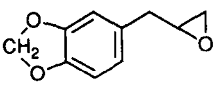
Chromium(III) heteropolytungstate complexes or their corresponding oxygenated forms were found to catalyze the oxidation of alkenes, alkanes, alcohols, and $Ph_3P$ at 50 °C by $OCl^-$, $H_2O_2$, or iodosobenzene [438]. The addition of 4 Å molecular sieves to the styrene epoxidation system consisting of *tert*-butyl hydroperoxide and **150** as the catalyst resulted in 96% conversion with 94% selectivity to styrene oxide [439].

The kinetics of epoxidation of 2-methyl-2-pentene with cumene hydroperoxide catalyzed by $MO_2(acac)_2$ was studied in the temperature range of 35–65 °C [440]. Alkylperoxo, alkoxo, peroxo and diolo molybdenum(VI) complexes formed in the course of catalytic epoxidation of cyclohexene with organic hydroperoxides [441] and hydrogen peroxide [442] were characterized with in situ $^{95}Mo$, $^{17}O$, $^{1}H$ NMR and EPR spectroscopy. The epoxidation of olefins and chloroolefins by *tert*-butyl hydroperoxide in the presence of $Mo(CO)_6$ as the catalyst was investigated [443]. The formation of intermediate complexes from (3-trifluoroacetylcamphorato) dioxomolybdenum and ethylphenyl hydroperoxide has been investigated in connection with the liquid phase epoxidation of alkenes by organic hydroperoxides catalyzed by molybdenum compounds [444]. 1-Octene and (*R*)-(+)-limonene were epoxidized by hydrogen peroxide in the presence of $[PM_4O_{24}]^{3-}$ and $[HPW_2O_{12}]^{2-}$ (M = Mo or W). The two anionic tungsten (VI) species were found to be ~30 times more active than the molybdenum(VI) complex [445]. Safrole and methyleugenol was epoxidized to **151** and **152**, respectively, with hydrogen peroxide in the presence of methyltrioctylammonium tetrakis(oxodiperoxotungsto)phosphate as the catalyst under two-phase conditions [446].

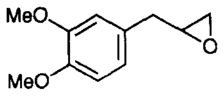
The epoxidation of cyclohexene with hydrogen peroxide was performed with



**150**



**151**

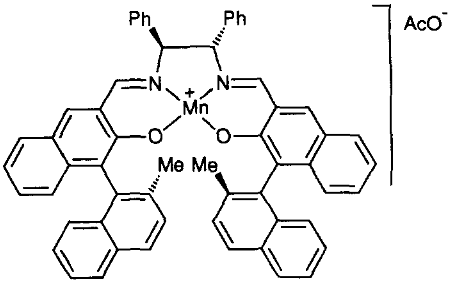


**152**

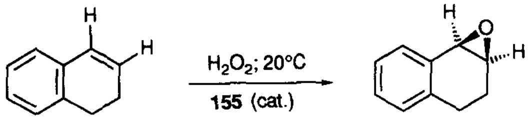
tungsten-based catalysts in the form of polymer supported pyridinium peroxotungstate salts and betaines [447]. The epoxidation of olefin by iodosobenzene was found to be catalyzed by α- and $\beta$-$K_6H_4[SiW_9O_{37}Mn_3(H_2O)_3]\cdot xH_2O$ [448]. Epoxidation of *cis* olefins such as dihydronaphthalene with iodosobenzene in the presence of pyridine *N*-oxide and **153** as the catalyst in acetonitrile give 77% yield of (1*S*, 2*R*)-1,2-epoxy-1,2,3,4-tetrahydronaphthalene in 86% ee [449].

The asymmetric epoxidation of 1,2-dihydronaphthalene with dilute hydrogen peroxide in the presence of **155** as the catalyst gave **154** in up to 72% yield and 64% ee [450].

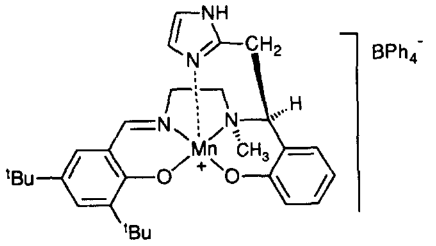
The asymmetric epoxidation reaction catalyzed by **156** was found to exhibit



**153**

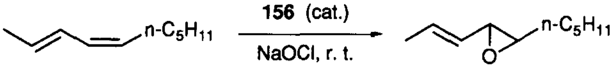


**154**



**155**

regioselectivity for attack at *cis* double bonds of conjugated dienes to afford enantiomerically enriched *trans*-vinyl epoxides as the major products [451]. E.g.:

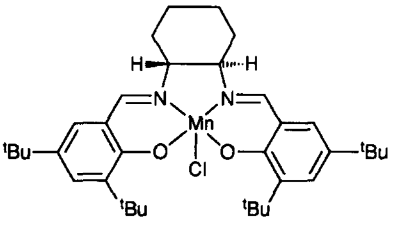


81% isolated yield
87% ee

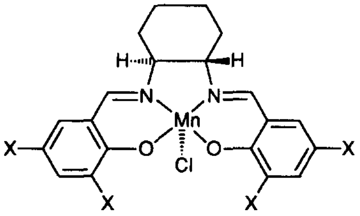
Low enantiomeric excess values were obtained in the enantioselective epoxidation of 1,3-cyclooctadiene and 4-chlorostyrene with NaOCl, $KHSO_5$ or $H_2O_2$ using **157** as the catalyst [452].

Catalytic epoxidation of different alkenes was reported using polymer supported Mn(III)-salen catalyst **158** in the presence of iodosobenzene as terminal oxidant [453].

The catalytic asymmetric epoxidation of styrene and 1-dodecene in 10% and 16%

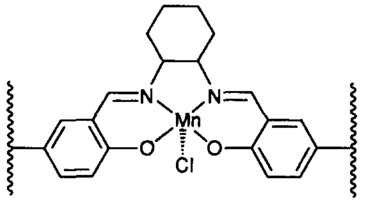


**156**



X = $^t$Bu, Cl, Br

**157**



**158**

ee, respectively, by NaOCl was catalyzed by *meso*-tetrafenchylidenylmethylporphyrinato manganese(III) at room temperature [454]. Epoxidation with iodosobenzene catalyzed by manganese porphyrins oriented both parallel and perpendicular to the director of a nematic liquid crystal have been studied [455]. Tailed manganese(III)-tetraarylporphyrins bearing an axial ligand and/or a carboxylic group was found to catalyze the epoxidation of alkene by NaOCl or $H_2O_2$ at 0 °C under aqueous $CH_2Cl_2$ two-phase conditions [456]. Alkenes (for example: cyclooctene, 4-acetyl-1-methyl-cyclohexene, styrene) were epoxidized with high yield (80–100%) in the presence of manganese(III) tetraphenylporphyrin-imidazol-sodium periodate-tetrabutylammonium-bromide system in methylene chloride-water media at room temperature [457]. The epoxidation of norbornene using manganese tetrakis 4-pyridyl- and tetrakis 3-pyridyl porphyrine acetate as the catalyst was investigated. The latter catalyst led selectively to exo-norbornene oxide in high yield [458].

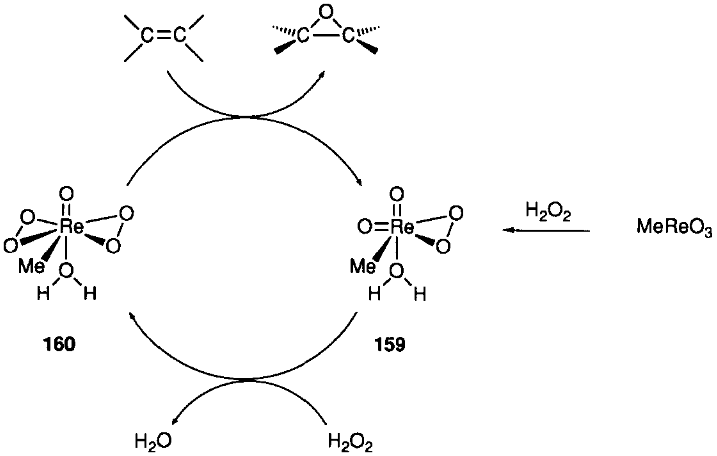
The catalytic activity of manganese phthalocyanine (MnPc) and zeolite Y encapsulated manganese phthalocyanine (MnPc–Y) was compared in epoxidation of olefins by PhIO. *cis*-Octene-2 was found to be more active in the MnPc-catalyzed epoxidation than the *trans* isomer. But for the MnPc–Y-catalyzed epoxidation much higher activity for *trans*-octene-2 than for *cis*-octene-2 was found [459].

Manganese picnic basket porphyrin catalysts, which have a rigid cavity of variable dimensions on one side of the porphyrin ring and a bulky anionic ligand on the other side showed dramatic selectivities in the epoxidation of several olefin pairs [460]. The manganese derivative of a threitol-strapped porphine was found to be the most effective asymmetric catalyst in the epoxidation of simple, monosubstituted olefins, and gave optical yields up to 88% ee in the epoxidation of *cis*-disubstituted olefins when iodosobenzene was the oxidant [461].

Nerol, *cis*-stilbene, and α-pinene were epoxidized by dioxygen in a two-phase system employing a manganese(III) tetraphenylporphyrin together with $Rh(\eta^5\text{-}C_5Me_5)(bipy)Cl_2$ as a redox-active phase transfer catalyst and sodium formate [462].

The mechanism of the catalytic epoxidation by the $MeReO_3/H_2O_2$ system was investigated. The observed reactivity of the isolated intermediates **159** and **160** support the following catalytic cycle [463].

The extent of $^{18}O$ incorporation into the products of metal complex-catalyzed epoxidation of cyclohexene and hydroxylation of cyclohexane using hydrogen peroxide, *tert*-butyl hydroperoxide, *m*-chloroperbenzoic acid, and iodosobenzene as oxidants, when $H_2{}^{18}O$ was added to the reaction mixture has been studied. The catalysts studied were (*meso-tetrakis*(2,6-dichlorophenyl)porphinato)iron)III) chloride with imidazole added, iron(II) cyclam (cyclam = 1,4,8,11-tetraazacyclooctatetra-decane), manganese(II) cyclam, and nickel(II) cyclam. In the case of iodosobenzene it was concluded that the mechanism for oxygen exchange does not involve metal oxo intermediates and that the observation of labeled oxygen from $H_2{}^{18}O$ into the products does not provide evidence for the intermediacy of metal oxo complexes [464]. The epoxidation of alkenes (*trans*-β-methylstyrene, *cis*-stilbene and *cis*-cyclooctene) with hydrogen peroxide at 40 °C was catalyzed by iron porphyrins immobilized to imidazole groups in a hydrophobic environment on a modified silica surface [465].



The asymmetric epoxidation of alkenes catalyzed by "chiral wall" metalloporphyrins was studied [466].

Stereoselective synthesis of 2,3-epoxy sulfoxides such as **161** and **162** was described applying a double enantioselective epoxidation of (*E*)-2-hexen-1-ol, followed by conversion to thioethers and asymmetric sulfur-oxidation [467].

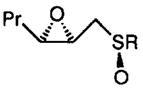
Long chain alkoxymethyl crown ethers were used as phase transfer catalysts in olefin epoxidation catalyzed by metalloporphyrins. More than 90% yield and ca. 100% selectivity was observed [468]. High-yield (60–100%) epoxidations of cyclooctene and norbornene were observed with hydrogen peroxide and *tert*-butyl hydroperoxide catalyzed by iron(III) tetrakis(pentafluorophenyl)porphyrin chloride and other electronegatively substituted porphyrins [469].

Asymmetric epoxidation of styrenes and related substituted olefins with iodosobenzene as an oxidant was performed in the presence of iron complexes of chiral bitetralin-linked "twin-coronet" porphyrins as the catalysts. Enantioselectivity between 54 and 96% ee was reported [470].

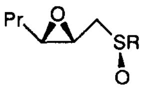
The kinetics of oxidation of some hydroxy acids by alkaline hexacyanoferrate(III) in the presence of ruthenium(III) were studied [471].

The asymmetric dihydroxylation of **163** in the presence of 9-*O*-(9′-phenanthryl)dihydroquinidine (**176**), $K_3Fe(CN)_6$, $K_2CO_3$ and $OsO_4$ gave a 84% yield of a 8:1 mixture of diols **164** and **165** [472].

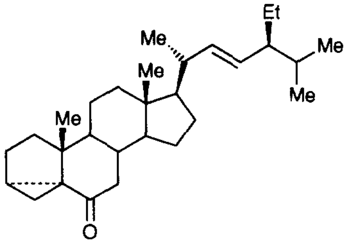
The large amount of *trans*-oxide versus *cis*-oxide (5.5:1) from the *cis*-stilbene epoxidation by [Ru$^{III}$(HEDTA)]/*tert*-butyl hydroperoxide, and 100% *trans*-oxide from *trans*-stilbene, was interpreted as indicative of a radicaloid intermediate in ⩾85% of the reaction channels [473].



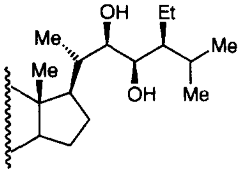
**161**



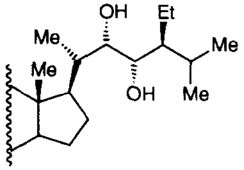
**162**



**163**



**164**



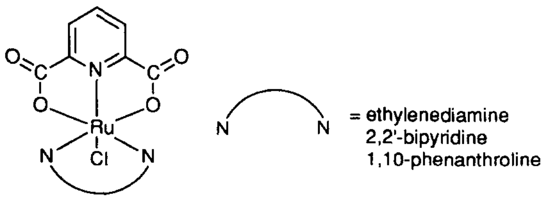
**165**

The mixed ligand complexes **166** were found to catalyze the epoxidation of various olefins at room temperature using iodosobenzene as the oxidant [474].

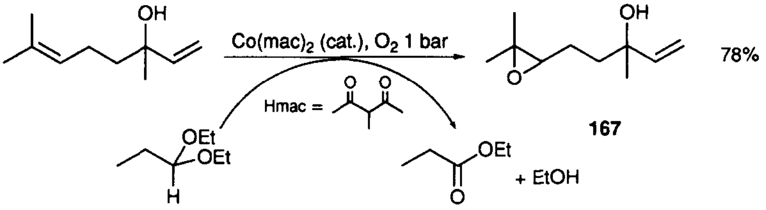
The asymmetric epoxidation of styrene with iodosobenzene in the presence of novel chiral ruthenium(II) Schiff base complexes as the catalysts has been studied. At low conversions (12–17%) 65–80% ee was observed [475].

The combined use of dioxygen and propionaldehyde dimethyl acetal in the Co(II)-catalyzed epoxidation of olefins was found to be useful in the preparation of acid-sensitive epoxide such as **167** or **168** [476].

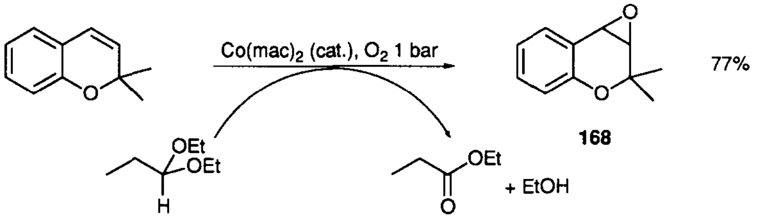
Copper(II) complexes containing *N*-glycoside ligands were found to catalyze the epoxidation of unfunctionalized olefins and (*E*)-cinnamyl acetate by *tert*-butyl hydroperoxide at room temperature. Low enantiomeric excess was observed [477]. The epoxidation of olefins with alkaline sodium bromite in the presence of copper sulfate was studied. Thus, the styrenes $PhCH=CH_2$ and $PhC(Me)=CH_2$ were found to give 75–89% yield of the corresponding epoxides [478]. The asymmetric catalytic epoxidations of simple olefin were studied [479]. See also Refs. [394,481,482,518].



**166**



**167**



**168**

### 4.5.3. Dihydroxylation of olefins

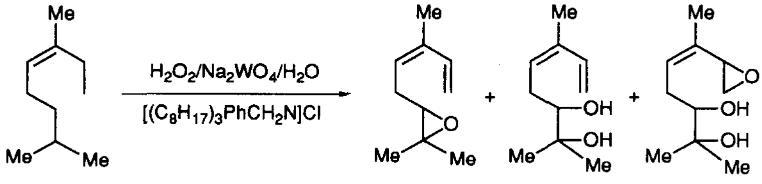
12-Molybdophosphate supported on low molecular weight poly(vinyl)pyridines was found to be an efficient catalyst for conversion of olefins into *vic*-diols with aqueous hydrogen peroxide in *tert*-butanol. On the other hand, supported peroxotungstophosphate catalyzed oxidative dehydrogenation of *sec*-alcohol function of alcohols and diols to the corresponding carbonyl compounds [480].

The $Na_2WO_4$-catalyzed epoxidation of **169** by hydrogen peroxide under phase-transfer catalyzed conditions gave **170**, **171**, and **172** [481].

In the case of the sodium tungstate-catalyzed hydroxylation of maleic acid by hydrogen peroxide, the formation of epoxysuccinic and tartaric acids, and the decomposition of hydrogen peroxide to molecular oxygen have been observed to take place in parallel. The mathematical model for the overall process has been developed [482].

Dihydroxylation of fluoroolefins gave up to 99% yields using stoichiometric amounts of $OsO_4$ or using hexacyanoferrate(III) as primary oxidant and $OsO_4$ as the catalyst [483]. The kinetics of the osmium(VIII)-catalyzed oxidation of allyl alcohol by hexacyanoferrete(III) in alkaline medium were sudied [484]. Vinyl- and allylsilanes were efficiently converted to the corresponding optically active vicinal diols in 6–88% ee with the osmium-catalyzed Sharpless asymmetric dihydroxylation [485].

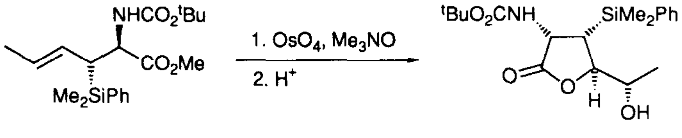
The osmium-catalyzed asymmetric polyhydroxylation of squalene to give a dode-



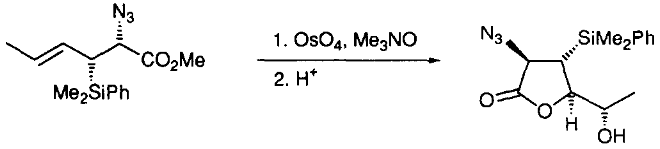
**169** **170** **171** **172**

cahydroxy derivative was found to be remarkably selective giving 1 out of the 36 possible stereoisomers in 78.9% overall yield [486].

Chiral crotylsilanes were converted in high yields and high diastereoselectivity into silyl-functionalized γ-lactones by the osmium tetroxide-catalyzed vicinal dihydroxylation using trimethylamine *N*-oxide as oxidant [487]. E.g.:



94% yield

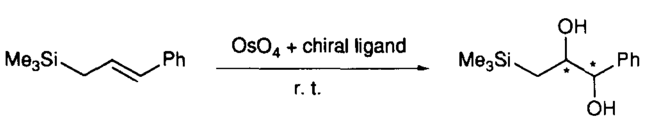


98% yield

The syntheses and crystal structures of the cinchona alkaloid derivatives **173**, **174**, **175**, and **176** — used as very effective ligands in the osmium-catalyzed asymmetric dihydroxylation of olefins — have been described [488].

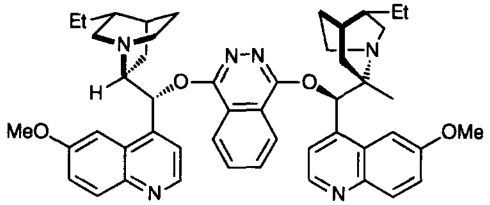
Bis-cinchona alkaloid substituted pyrimidine ligands were found to give improved enantioselectivity in the osmium tetroxide-catalyzed asymmetric dihydroxylation of monosubstituted terminal olefins. Thus, using 1 mol% of **177** and 1 mol% of $OsO_4$ in the presence of $K_3Fe(CN)_6$ in *tert*-butanol:$H_2O = 1:1$ at 0 °C gave 92% ee of (*R*)-3,3-dimethyl-1,2-butanediol in 80% yield from 3,3-dimethyl-1-butene [489].

The catalytic asymmetric dihydroxylation of tetrasubstituted olefins by $K_3Fe(CN)_6/OsO_4$ in the presence of pyrimidine-type or phthalazine-type chiral ligands resulted in products with 20–97% ee [490]. Allylic silanes were dihydroxylated using the Sharpless asymmetric dihydroxylation reaction [491]. E.g.:

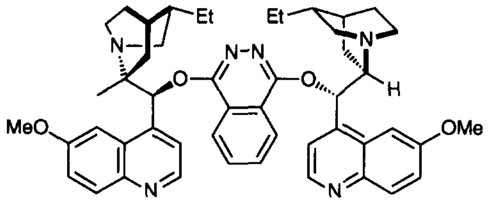


Phthalazine- (**178**) and pyrimidine-type (**179**, **180**) ligands were evaluated for their ability to achieve double diastereoselection in asymmetric dihydroxylation of the unsaturated ester **181**. The new ligands **178**, **179**, and **180** gave improved double diastereoselection and the product ratio **182**:**183** could be varied between 39:1 and 1:7 [492].

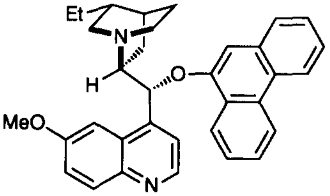
The asymmetric dihydroxylation of tertiary allylic alcohols using **173** (4 mol%), $K_2OsO_2(OH)_4$ (0.2 mol%), $K_3Fe(CN)_6$ (3 mol), $K_2CO_3$ (3 mol), and $MeSO_2NH_2$ at room temperature in *tert*-butyl alcohol-water (1:1) was investigated. Good to



**173**



**174**



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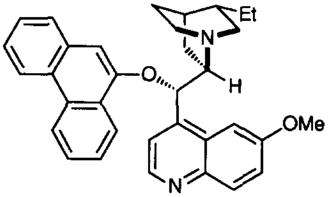
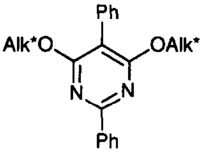
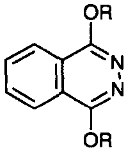


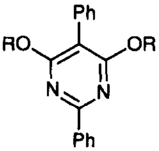
**176**

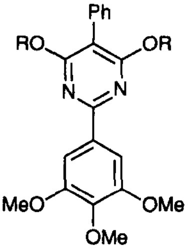


Alk* = dihydroquinidinyl or dyhydroquininyl

**177**

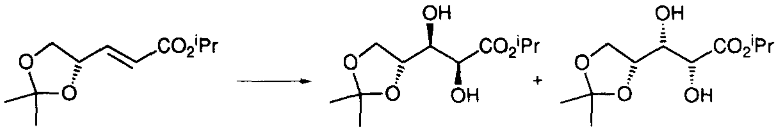






R = dihydroquinidinyl or dihydroquininyl

**178** **179** **180**

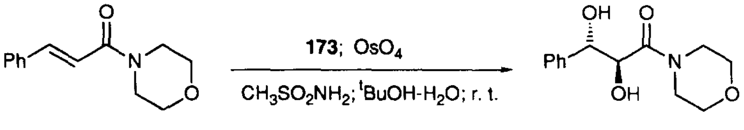


**181** **182** **183**

excellent enantioselectivities were obtained with *trans*-di- and tri-substituted tertiary alcohols [493]. E.g.:

83% yield, 91% ee

Asymmetric dihydroxylation of $\alpha,\beta$- and $\beta,\gamma$-unsaturated amides by a modified potassium osmate reagent containing **173** as a chiral ligand was found to afford the corresponding diols in good yields and excellent enantiomeric excesses [494]. E.g.:



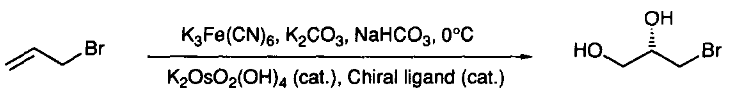
97% yield, 97% ee

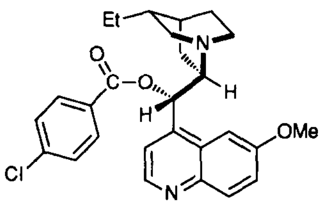
The origin of high enantioselectivity in the dihydroxylation of olefins using osmium tetroxide and cinchona alkaloid catalysts has been investigated. Based on kinetic results it was suggested that these dihydroxylations proceed by way of the $\mu$-oxo-bridged bis-Os(VIII) species in which the dihydroquinine or dihydroquinidine ether ligand is bonded to hexacoordinate osmium at the basic bridgehead nitrogen [495]. The observed kinetics was found to be first-order in both alkene and $OsO_4$ concentration and this result contradicts the idea of involvement of a $\mu$-oxo-bridged bis-$OsO_4$ species in the osmium tetroxide-catalyzed asymmetric dihydroxylation of olefins [496].

The asymmetric dihydroxylation of stilbene by treatment with osmium tetroxide in the presence of 4-methylmorpholine *N*-oxide and **184** in acetone/water solution gave diol **185** in 90% yield [497].

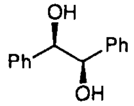
The regioselective asymmetric dihydroxylation has been applied for converting **186** into **187** by a solution of **173**, $K_3Fe(CN)_6$, $K_2CO_3$, $MeSO_2NH_2$, and $OsO_4$ in *tert*-butanol/water [498].

In the presence of 1 mole % of sterically encumbered dihydroquinidine the catalytic asymmetric dihydroxylation of allyl bromide gave enantiomerically enriched (*S*)-(+)-3-bromopropane-1,2-diol in 72% ee [499].

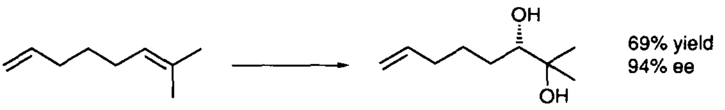




**184**



**185**



**186** **187**

The relationship between the % ee and variation of the substituents in the aromatic ring when aryl allyl ethers are subjected to asymmetric dihydroxylation using the commercially available AD-mix-$\beta$ reagent was studied. *Para*-substituents were found to give 89–95% ee while ortho-groups only 28–63% ee. From 1-naphthyl allyl ether the corresponding (*R*)-diol was obtained in 90% yield and 91% ee [500].

Dihydroquinidine and dihydroquinine diesters of malonic, adipic, and terephthalic acid were used as chiral auxiliaries for osmium tetroxide-catalyzed asymmetric dihydroxylation of alkenes were rationalized on the basis of $\pi$–$\pi$ interaction of the alkenes with the ligand [501].

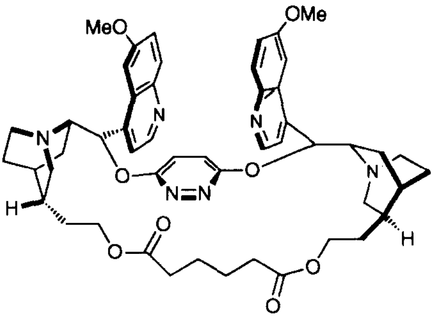
A macrocyclic bis-quinidine derivative **188** was used as chiral ligand in the osmium tetroxide-catalyzed dihydroxylation of various olefins (1 mol% ligand, 0.1 mol% $K_2OsO_4$, 3 equiv $K_3Fe(CN)_6$, 3 equiv $K_2CO_3$, in 1 : 1 *tert*-butyl-alcohol/water, 0 °C). Excellent enantioselectivities and yields were obtained in the dihydroxylation of (*E*)-stilbene (>99% ee, 99% yield) and 1-phenylcyclohexene (95% ee, 88% yield), which are parallel to those obtained with the unbridged ligand. The origin of enantiospecifity has been discussed [502]. See also Ref. [545].

### 4.5.4. *Oxidation of O-containing functional groups*

Benzyl alcohol was oxidized to benzaldehyde using hydrogen peroxide as an oxidation agent and cerium nitrate as a catalyst in acetic acid or trichloroacetic acid solution between 55 and 90 °C [503].

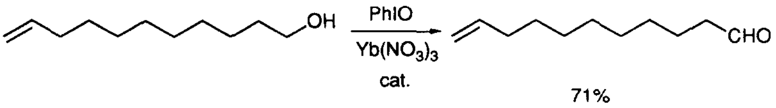
The kinetics of oxidation of cyclohexanol with hydrogen peroxide to cyclohexanone in the presence of the heteropolytungstolanthanate anion ($Ce^{IV}W_{10}O_{36}^{8-}$, $Nd^{III}W_{10}O_{36}^{9-}$, and $Sm^{III}W_{10}O_{36}^{9-}$) were investigated [504].

Treatment of 1,2-dichloroethane solution of various alcohols with iodosobenzene at 80 °C in the presence of a catalytic amount of ytterbium(III), terbium(III),



**188**

holmium(III) or lutetium(III) nitrate provided the corresponding carbonyl compounds selectively in good to excellent yields [505]. E.g.:



In connection with lignin degradation the oxidation of **189** and other dimethoxyarenes as lignin models by hydrogen peroxide, $C_6F_5IO$, or magnesium monoperoxyphthalate in the presence of various iron(III) porphyrins was studied [506].

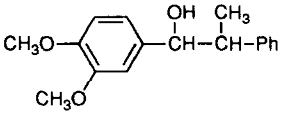
In pyridine solution $Fe(bpy)_2^{2+}$ was found to activate hydrogen peroxide for the efficient and selective catalytic oxidation of veratryl alcohol [507].

The oxidation of alcohols $R^1CH(OH)R^2$ ($R^1=Ph$, $R^2=Me$, Ph, $CO_2Me$; $R^1=CH_2Ph$, *trans*-PhCH=CH, $R^2=Me$; $R^1=$*trans*-MeCH=CH, $R^2=n\text{-}C_5H_{11}$) to the corresponding carbonyl compounds $R^1COR^2$ with *tert*-butyl hydroperoxide was found to be catalyzed by dichlorotris(triphenylphosphine)ruthenium with high efficiency. This method can be applied to the oxidation of $R^3CH(OH)CN$ ($R^3=Ph$, 2-$MeOC_6H_4$, 1-naphthyl, etc.) to give $R_3COCN$ [508].

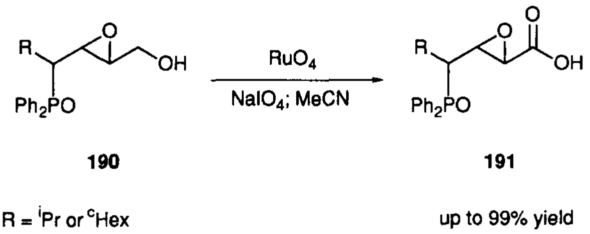
Primary and secondary alcohols were oxidized to the corresponding aldehyde and ketone with high selectivity by aqueous persulfate in the presence of catalytic amounts of ruthenium complexes. For example the persulfate oxidation of cyclooctanol gave 99% yield of cyclooctanone at 22 °C in the presence of $[RuCl(dppp)_2]PF_6$ as the catalyst [509].

Oxidation of various stereoisomers of **190** by $NaIO_4$ in the presence of $RuCl_3$ in MeCN gave the corresponding epoxy acids **191** in excellent yield [510].

Ruthenium trichloride was found to be an active catalyst for the oxidation of



**189**



**190**

**191**

alcohols to carbonyl compounds with *tert*-butyl hydroperoxide [511]. The kinetics of ruthenium(III)-catalyzed oxidation of aliphatic aldehydes by bromamine-T were studied in aqueous medium over a wide acid range [512]. The kinetics of the ruthenium(III)-catalyzed oxidation of 3-methylcyclohexanol by *N*-bromosuccinimide were investigated in perchloric acid media in the presence of mercuric acetate [513]. The kinetics of ruthenium tetroxide-catalyzed oxidation of glycerol and erythritol by *N*-bromoacetamide were studied in alkaline media in the presence of mercuric acetate [514]. The kinetics of ruthenium(III)-catalyzed *N*-bromoacetamide oxidation of adonitol were investigated in perchloric acid medium in the presence of mercuric acetate as a bromide scavenger [515]. The kinetics of the oxidation of isobutanol by hexacyanoferrate(III) in alkaline media were studied using ruthenium(III) chloride as the catalyst precursor [516].

Primary alcohols, activated alkyl halides, aldehydes, 1,2-diols, and nitroalkanes were oxidized to carboxylic acids, while secondary alcohols and secondary halides were oxidized to ketones by bromate in the presence of perruthenate anion as the catalyst. These oxidations were compared with those effected catalytically by *trans*-$[Ru(OH)_2O_3]^{2-}$ in aqueous base at pH 14 with persulfate as cooxidant [517].

The cobalt(II)-catalyzed reaction of aldehydes with acetic anhydride under a dioxygen atmosphere was investigated. Depending upon the reaction medium, carboxylic acids and 1,2-diones were obtained. In the absence of acetic anhydride aliphatic aldehydes give the corresponding anhydrides. The cobalt(II)-catalyzed reaction of isobutyraldehyde in the presence of *trans*-stilbene and dioxigen results in the formation of stilbene oxide and isobutyric anhydride in excellent yield [518].

The oxidation of ascorbic acid by chromium(VI) was found to be catalyzed by traces of copper(II). The copper(II) catalysis occurs via complexation of the catalyst with the substrate [519]. The iridium(III)-catalyzed oxidations of 1,2-ethanediol and 1,4-butanediol to the corresponding dicarboxylic acids by *N*-bromoacetamide were investigated in $HClO_4$ in the presence of $Hg(OAc)_2$ as a scavenger for bromide ion [520].

The platinum(II)-catalyzed oxidation of simple cyclic ketones with hydrogen peroxide to give the corresponding lactones was reported. Based on initial rate studies the mechanism of the reaction was studied [521].

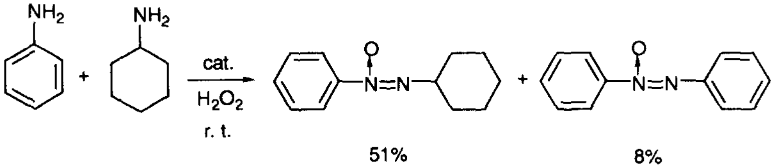
The catalytic oxidation of primary and secondary alcohols to the corresponding aldehyde and ketone, respectively was achieved by using a combination of bis(bipyridine)copper(II) and two equivalents of a base ($HO^-$ or $HOC(O)O^-$) in a dioxygen-saturated acetonitrile solution. The build up of water (the byproduct) deactivates the catalyst via its reduction to the copper(I) state. In the absence of alcohol, the catalyst initiates the auto-oxygenation of aldehydes to carboxylic acids [522]. α-Chloro (or α-bromo, or α-iodo) adipic acid was prepared in good yield by oxidative cleavage of 1,2-cyclohexanedione with 30% hydrogen peroxide using copper(II) halide (or $CuSO_4 \cdot 5H_2O$ and NaI) as the catalyst in the presence of alkali metal halide [523].

The kinetics and mechanism of silver(I)-catalyzed oxidation of malonic acid to glyoxylic acid and $CO_2$ by peroxodiphosphate in acetate buffers were investigated [524]. See also Refs. [230,356,438,480].

### 4.5.5. *Oxidation of N-containing organic compounds*

The oxidation of primary aromatic amines to the corresponding nitroso compounds by hydrogen peroxide was found to be catalyzed by $Mo(O)(O_2)_2(H_2O)(HMPA)$ (HMPA = hexamethylphosphoric triamide) at room temperature. Total conversion of the amine and 40–80% yield of the nitroso compounds was observed [525]. The catalytic oxidation of cyclohexylamine by aqueous hydrogen peroxide to cyclohexanone oxime, cyclohexanone, and nitrocyclohexane was observed in the presence of $Mo(O)(O_2)_2(H_2O)(HMPA)$ at room temperature. The best results show an amine conversion of 40% [526].

The oxidation of anilines with 35% hydrogen peroxide in the presence of catalytic amount of cetylpyridinium peroxotungstophosphate, $[\pi\text{-}C_5H_5N^+(CH_2)_{15}CH_3]_3$—$\{PO_4[W(O)(O_2)_2]_4\}^{3-}$, at room temperature in chloroform under two-phase conditions was found to afford nitrobenzenes with high (up to 85%) selectivity. When the reaction was carried out in refluxing chloroform, nitrobenzenes were obtained in good yield (63–95%). The cooxidation of aniline and aliphatic primary amines provided a direct route to phenylazoxyalkanes [527]. E.g.:



The specific cleavage of right-handed double-helical DNA in regions rich in A:T base pairs has been achieved by using a combination of $[SalenMn(III)]^+$ catalyst (Salen = *N*, *N*′-ethylenebis(salicylideneaminato) and magnesium monoperoxyphthalate as a terminal oxidant [528].

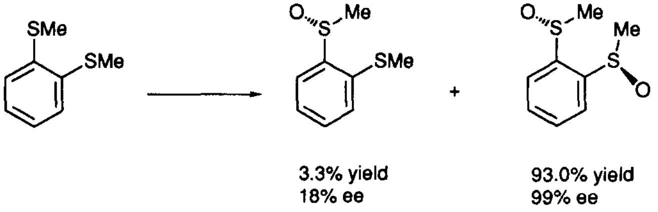
The oxidation of primary aromatic amines to nitro derivatives by *tert*-butyl hydroperoxyde catalyzed by iron(III) and manganese(III) tetraaryl porphyrins was reported. Turnovers of up to 18000 per hour were achieved [529].

The kinetics of oxidation of monoethanolamine, diethanolamine and triethanolamine by Tl(III) with Ru(III) as the catalyst were studied in acetic acid water mixture. The products of the reaction were found to be formaldehyde and ammonia. A mechanism involving formation of an adduct between the catalyst and the substrate in a fast step which reacts later with the oxidant in a slow step to give the products was proposed [530].

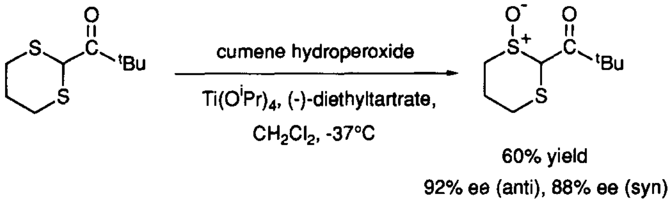
The kinetics of the osmium tetroxide-catalyzed oxidation of alanine by chloramine-T in alkaline medium were studied. The reaction was found to be first-order with respect to both chloramine-T and alanine, negative first-order in sodium hydroxide and fractional-order in osmium tetroxide [531]. See also Refs. [517, 624].

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

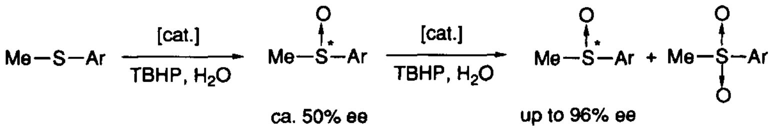
The oxidation of bis-methylthioethers by *tert*-butyl hydroperoxide, titanium tetra-iso-propylate, and (+)-diethyltartrate, afforded the almost enantiomerically pure *dl*-bis-methylsulfinylbenzenes (ee ⩾99%) [532]. E.g.:



The asymmetric oxidation of 1,3-dithiane derivatives by cumene hydroperoxide in the presence of a chiral titanium alkoxide catalyst gave the corresponding oxides as *syn*/*anti* mixtures in reasonable yields and with good to excellent enantiomeric excesses [533]. E.g.:



The complex derived from Ti(O*i*Pr)$_4$ and binaphthol was found to catalyze the asymmetric oxidation of sulfides by *tert*-butyl hydroperoxide as well as the kinetic resolution of sulfoxides [534].

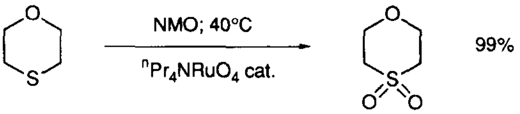


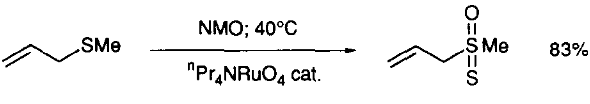
In the kinetic resolution using (*R*)-(+)-binaphthol/Ti(O$^i$Pr)$_4$/H$_2$O = 0.1/0.050/1.0 mol equiv relative to the racemic methyl *p*-tolylsulfoxide, 1.0 mol equiv of commercial 70% aqueous *tert*-butyl hydroperoxide at 25 °C, higher than 99% ee of the (*R*)-sulfoxide was isolated [535].

The hydrolytically stable organic triester capped polyoxometalate complex $[CH_3C(CH_2O)_3V_3P_2W_{15}O_{59}]^{6-}$ was found to catalyze the rapid and selective oxidation of tetrahydrothiophene to the corresponding sulfoxide by *tert*-butyl hydroperoxide, hydrogen peroxide, or iodosobenzene in acetonitrile at 40 °C [536]. The kinetics of oxidation of dimethyl sulfoxide by aqueous hydrogen peroxide catalyzed by sodium molybdate in acid medium were investigated at 40 °C [537].

The complex $2Bu_4N^+[Fe_4S_4(SPh)_4]^{2-}$ was found to catalyze the oxidation of benzenethiol to diphenyl disulfide with the reduction of dioxygen to water [538].

Tetrapropylammonium perruthenate was found to be an efficient catalyst for the chemoselective conversion of sulfoxides to sulfones by *N*-methylmorpholine-*N*-oxide at 40 °C. Isolated double bonds are generally unaffected in the reaction [539]. E.g.:





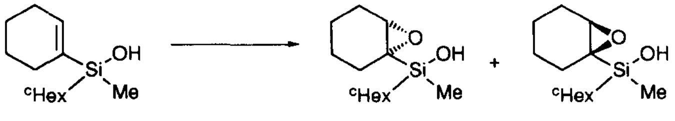
See also Refs. [438,467,517].

### 4.5.7. Kinetic resolution by asymmetric oxidation

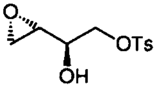
The kinetic resolution of racemic cyclohex-1-enylsilanols by the Sharpless asymmetric epoxidation was studied. Using (−)-dicyclododecyl tartrate with $Ti(OEt)_4$, *tert*-butyl hydroperoxide and molecular sieve 4 Å, from racemic **192** at 71% conversion (*R*)Si-**192** with >99% ee was obtained. The ratio of diastereomers **193**:**194** was found to be 95:5 [540].

The (*S*)- and (*R*)-enantiomers of α-furfuryl amides were obtained with 90–100% ee and 45–50% yield by kinetic resolution of the racem $2\text{-}C_4H_3OCHRNHTs$ ($2\text{-}C_4H_3O$ = furyl group) using the modified Sharpless asymmetric epoxidation reagent (*tert*-butyl hydroperoxide, $Ti(O^iPr)_4$, and L-(+) or D-(−)-diisopropyltartrate) [541].

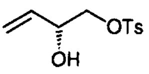
Enantiomerically pure **195** and **196** or **197** and **198** were prepared from racemic 1-tosyloxy-3-butene-2-ol using kinetic resolution under Sharpless epoxidation conditions [542].



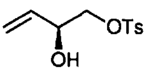
**192** **193** **194**



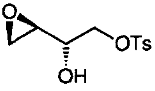
**195**



**196**



**197**

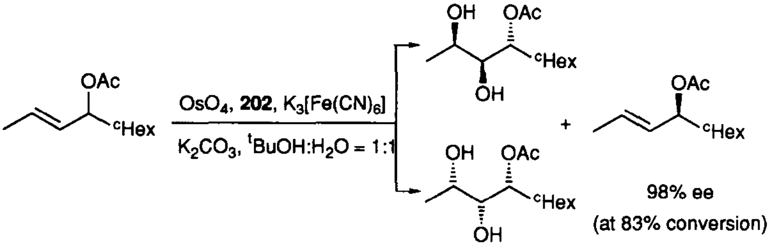


**198**

The Sharpless kinetic resolution was applied to obtain *R*-**199** from racemic **199** [543].

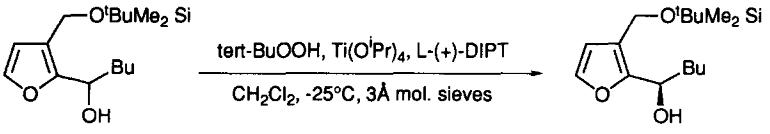
Kinetic resolution of axially dissymmetric alkenes via asymmetric dihydroxylation using the commercially available AD-mixes was demonstrated in the case of **200** and **201** [544].

The kinetic resolution of several racemic allylic acetates were examined using osmium tetroxide-cinchona alkaloid as chiral catalyst [545]. E.g.:



98% ee
(at 83% conversion)

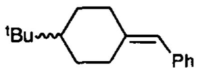
The chiral fullerene $C_{76}$ was kinetically resolved by asymmetric osmylation. $C_{76}$ with $OsO_4$ and a chiral alkaloid ligand, showed a specific rotation $[\alpha]_D$ of −4000 °C corresponding to >97% ee. The regenerated $C_{76}$ formed by reducing the osmylated $C_{76}$ with $SnCl_2$ was found to be enriched in the opposite enantiomer [546]. See also Refs. [534, 535].



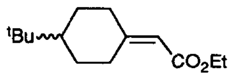
**199**

41% yield, >95% ee

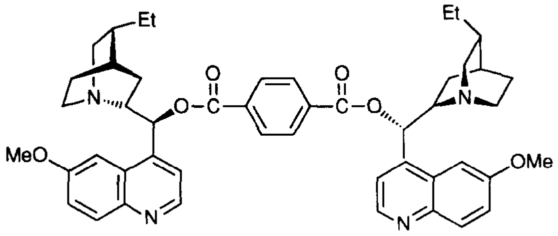
R-**199**



**200**



**201**

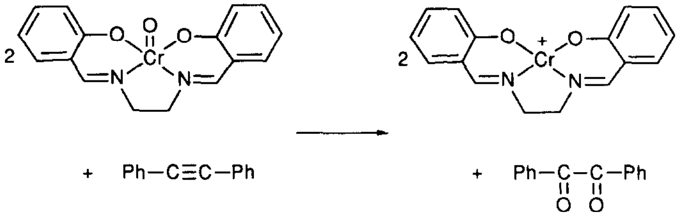


**202**

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

#### 4.6.1 Oxidation of hydrocarbons or hydrocarbon groups

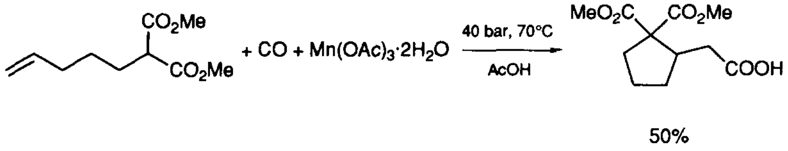
Alkynes were oxidized by oxo(salen)chromium(V) triflate to form 1, 2-diones. For example, diphenylacetylene afforded benzil in 87% yield. This reaction was found to be first-order in oxometal complex and first-order in alkyne. It was suggested that an intermediate, most likely a metallaoxetane or a related species, such as a metallocarbene, formed in the rate-determining step reacts fast with a second equivalent of oxometal complex to form benzil [547].

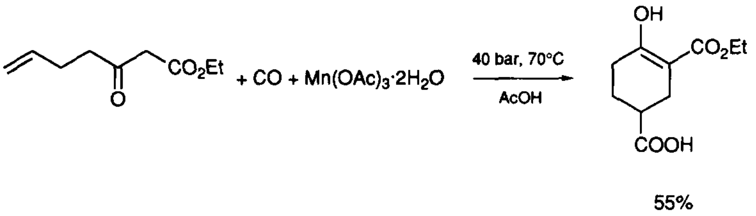


The kinetics of oxidation of styrene and substituted styrenes to the corresponding benzaldehyde and formaldehyde by quinolinium dichromate in dimethyl formamide, in the presence of an acid, was investigated. The rate of the the reaction was found to be dependent on the first powers of the concentrations of substrate, oxidant, and acid. Correlation of the rate constants with s substituent constants gave a value of $\rho = -4.0$. The oxidation of $\beta,\beta$-dideuteriostyrene gave an inverse secondary kinetic isotope effect ($k_H/k_D = 0.80$) [548].

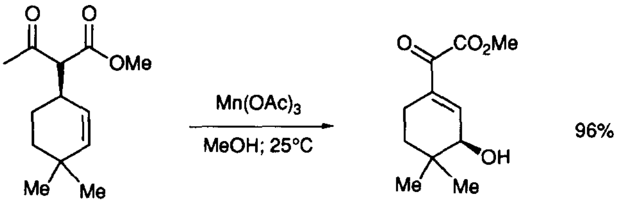
Both cyclic and acyclic dienes were found to react with the pyridinium dichromate — *tert*-butyl hydroperoxide reagent system at 0 °C to give 4-*tert*-butyldioxy-2-enones in up to 76% yield [549]. Ammonium chlorochromate was used to oxidize α-methyl or α-methylene groups in carbonyl compounds. Thus, treatment of acetophenone with ammonium chlorochromate in DMF at 75 °C afforded PhCOCHO in 80% yield [550]. Chromyl chloride was used in a variety of transformations such as the preparation of chromate ester oxidant, the Etard aryl-alkane C–H oxidation and olefin oxychlorination. The ditertiary chromate esters derived from chromyl chloride and tert-butyl alcohol, and 2, 4-dimethyl-2, 4-pentanediol were utilized in the oxidation of several alcohols to carbonyl compounds [551].

Carbon monoxide was trapped in a manganese(III)-induced oxidation system [552]. E.g.:





Manganese(III) salen complexes attached to steroid substrates were found to mediate the hydroxylation of unactivated carbons with iodosobenzene as the oxygen atom source [553]. Various α-allyl-β-keto esters were oxidized by $Mn(OAc)_3$ at 25 °C to the corresponding δ-hydroxy-β, γ-unsaturated-α-keto ester in good yields [554]. E.g.:



Oxidation of $4\text{-}MeC_6H_4OCCH_2C{\equiv}CH$ and $BuC(OH)MeC{\equiv}C(OH)MeBu$ in acetone solution by an aqueous solution of $KMnO_4$ containing $NaHCO_3$ and $MgSO_4$ gave $4\text{-}MeC_6H_4OCH_2COCHO$ and $BuC(OH)MeCOCOC(OH)MeBu$ in 70 and 68% yield, respectively [555]. Permanganate absorbed on moist alumina was found to cleave the carbon–carbon bond of olefins affording aldehydes in up to 95% yield [556].

Mononuclear $[FeX_2(TPA)]^+$ complexes (TPA = tris(2-pyridylmethyl)amine; X = Br, Cl, or $N_3$) were found to effect stoichiometric functionalization of cyclohexane by oxidative ligand transfer. Thus, treatment of the mononuclear halo-complexes with an excess of alkyl hydroperoxyde in the presence of cyclohexane affords halocyclohexane in up to 100% yield based on the complex. In the proposed mechanism the active species $[O{=}Fe(TPA)X]^{2+}$ abstracts hydrogen from the alkane and then transfers the bound halide to the incipient alkyl radical [557].

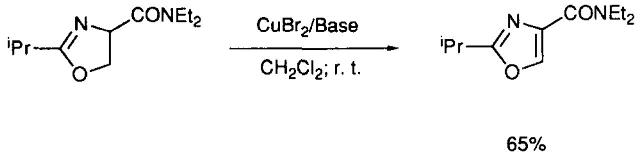
Barium ruthenate, $BaRu(O)_2(OH)_3$ in acetic acid-dichloromethane was found to oxidize cyclohexane, adamantane, *n*-hexane, ethylbenzene, THF, cyclohexanol and triphenylphosphine to afford cyclohexanone, a mixture of hexan-2-one and hexan-3-one, acetophenone, γ-butyrolactone, cyclohexanone and triphenylphosphine oxide at 23 °C in good to excellent yields. The oxidation could be made catalytic by using $^{n}Bu_4NIO_4$ as terminal oxidant. Higher rates but lower selectivity was observed in the presence of Lewis acids [558].

The kinetics of the side-chain oxidation of α-substituted 4-methoxytoluenes by $K_5Co^{III}W_{12}O_{40}{\cdot}H_2O$ in $AcOH/H_2O$ (55:45) were studied [559].

The mechanism of the oxidation of 1-methylcyclobutene to cyclopropyl methyl ketone [560] and methylenecyclobutane to cyclopentanone [561] by $PdCl_2(CD_3CN)_2$ and $PdCl(NO_2)(CD_3CN)_2$ in methylene chloride was investigated by in situ $^1H$ and $^{13}C$ NMR spectroscopy.

Water-soluble organic compounds such as *p*-toluenesulfonic acid were selectively oxidized by aqueous solutions of chloroplatinum(II) and chloroplatinum(IV) salts to the corresponding alcohol and aldehyde [562].

4-Carboxyoxazolines were oxidized to the corresponding oxazoles in a cupric bromide mediated reaction at room temperature [563]. E.g.:

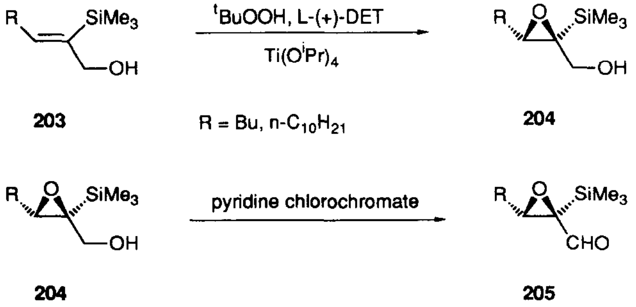


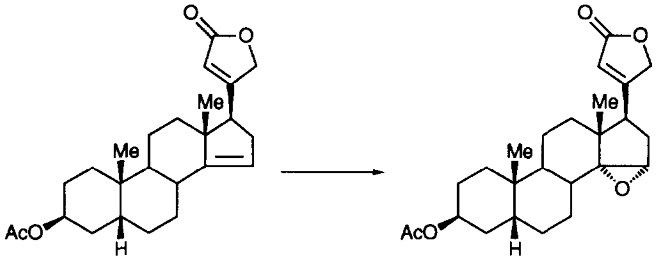
### 4.6.2. *Epoxidation and dihydroxylation of olefins*

Aqueous solutions of triperoxovanadium(V) complexes were found to oxidize α,β-unsaturated ketones to the corresponding epoxides, and benzil to benzoic acid [564]. The Sharpless asymmetric epoxidation of **203** gave **204** in 94% yield and 97% ee.

The epoxidation of **206** with chromyl diacetate in methylene chloride gave **207** in 78% yield [566].

Monoenoic fatty esters were epoxidized by cumyl hydroperoxide in the presence of hexacarbonylmolybdenum giving 100% yields in most cases. Also examined was the use of chromium and cobalt carbonyls and *tert*-butyl hydroperoxide [567]. Oxoperoxomolybdenum(VI) complexes obtained by the reaction of $MoO_2L{\cdot}nMeOH$





**206** **207**

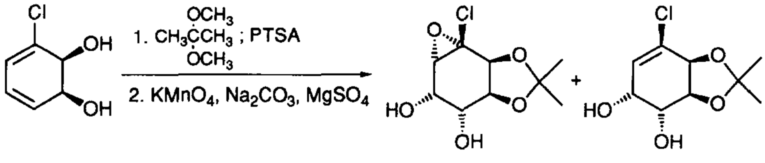
($LH_2 = (HOCH_2CH_2)_2NH$, $(HOCHMeCH_2)_2NH$; $n = 1$, 0, respectively) with *tert*-butyl hydroperoxide were found to epoxidize cyclohexene [568].

The mechanism for the reaction of *meso*-tetrakis(2,6-dichlorophenyl)porphinato-oxo-manganese(VI) with alkenes was investigated by kinetics and product identification [569]. Treatment of **208** with 2,2-dimethoxypropane/PTSA and subsequent addition of $KMnO_4/MgSO_4$ in aqueous acetone at −10 °C to 5 °C gave an 8:1 mixture of diols **209** and **210** in 60% yield [570].

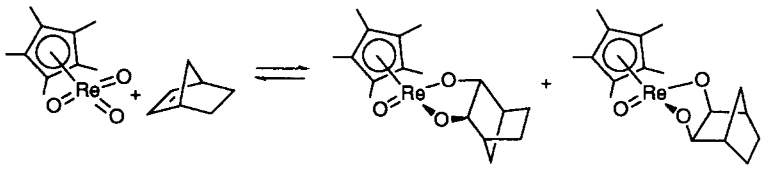
A kinetic study of the selective oxidation of the thymine residue of oligonucleotides by potassium permanganate has revealed that electrostatics rather than conformation control the oxidation [571].

The oxidation of alkenes by technetium(VII) oxo complexes was studied [572]. The temperature dependence of the reversible oxidation of norbornene by **211** was studied by NMR spectroscopy, and gave $\Delta H° = -10.9 \pm 0.9$ kcal mol$^{-1}$ and $\Delta S° = -22.8 \pm 2.2$ eu for the equilibrium [573].

The oxo-iron(V) complex $O{=}Fe^V(Cl_8TPP)(MeOH)$ was found to oxidize norbornene to the epoxide at −90 °C in a rection that is first-order in each reactant and that proceeds at $1.3 \times 10^{-3}$ s$^{-1}$ [574]. The kinetics of alkene oxidation by a series of isostructural cationic *trans*-dioxoruthenium(VI) complexes with E°($Ru^{VI}$–$Ru^V$) ranging from 0.23 to 0.7 V vs. SCE were studied in acetonitrile. The experimental



**208** **209** **210**

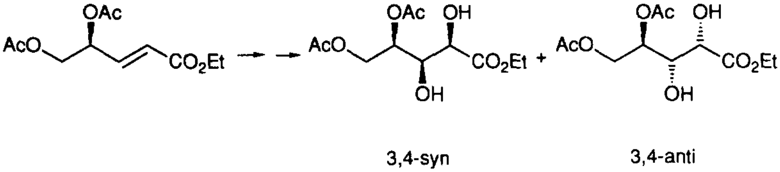


**211** major minor

rate law was found to be rate $= k_2$[alkene][$Ru^{VI}$]. For the oxidation of *para*-substituted styrenes a $\rho$ value of $-2.1$ was found [575].

The diamine **212** was found to be an effective ligand for the stoichiometric dihydroxylation of a variety of aliphatic and aromatic di- and tri-substituted olefins with osmium-tetroxide. The corresponding diols were obtained with 64–99% ee [576].

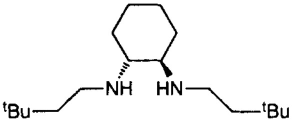
Dihydroxylation of chiral α,β-unsaturated esters at −78 °C with a stoichiometric amount of osmium-tetroxide-diamine complex was investigated. Highly diastereoselective dihydroxylation of 4,5-dihydroxy-2-pentenoate was observed using chiral *N,N′*-dialkyl-2,2′-bipyrrolidine as ligands. Either *syn* or *anti* selection was achieved by employing the enantiomeric ligands with more than 90% yields [577].



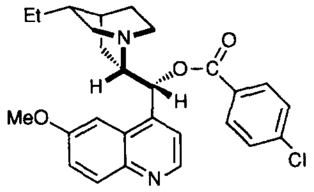
The dihydroxylation reaction with osmium tetroxide-pyridine, osmium tetroxide-**213**, and osmium tetroxide-**184** was applied in the synthesis and structure elucidation of Gerardiasterone [578].

The kinetics and mechanism of the dihydroxylation of aryl β-styryl ketones by osmium tetroxide in sulfuric acid-acetic acid medium have been studied. The order of reactivity of $XC_6H_4COCH{=}CHPh$ is (X =): 4-Me > H > 4-Cl > 3-Cl > 4-$NO_2$ and gives $\rho^+ = -0.33$ [579]. The kinetics of osmim tetroxide oxidation of maleic, fumaric, cinnamic, and crotonic acid in aqueous alkaline medium were studied by spectrometric stopped flow technique [580].

From the effect of temperature on the stoichiometric asymmetric olefin dihydroxylation by osmium tetroxide/chiral ligand a step by step [2+2] mechanism was suggested [581]. See also Ref. [540].



**212**



**213**

### 4.6.3. Oxidation of O-containing functional groups

The kinetics of oxidation of benzaldehyde and substituted benzaldehydes with ceric ammonium nitrate in acetonitrile were studied. The oxidation was found to be overall second order, first-order each in acetal and cerium(IV) concentration [582]. The kinetics and mechanism of the oxidation of phenols by the oxochromium(IV) ion was investigated. The oxidation yields *p*-benzoquinone as a major product, and was found to be first-order in $CrO^{2+}$ and first-order in phenol. Deuteration of the hydroxylic hydrogen resulted in a large kinetic isotope effect, $k_H/k_D = 14.7$. No kinetic isotope effect was found in the case of deuteration of the C–H hydrogen. A mechanism was proposed according to which the phenols are first oxidized by one electron to the corresponding phenoxyl radicals and then the superoxochromium(III) ion oxidizes the phenoxyl radicals to benzoquinones [583].

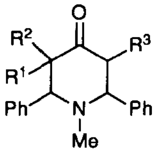
The kinetics of oxidation of **214** by pyridinium fluorochromate in aqueous acetic acid at fixed sulfuric acid concentration were studied iodometrically under pseudo first-order conditions at 35–50 °C. The reaction was found to be first-order each with respect to **214** and oxidant [584]. The kinetics and linear free energy relations of the oxidation of nine mandelic acid derivatives by pyridinium fluorochromate to the corresponding arylglyoxylic acids were studied [585]. The kinetics of oxidation of benzoin by quinolinium dichromate was studied. The reaction showed a first-order dependence on the concentrations of each substrate, oxidant, and acid [586].

The oxidation of $PhCH_2OH$ or ROH ($R = Me_2CH$, Bu, *n*-hexyl, *n*-octyl) by chromium(VI) was used as a laboratory exercise for determining kinetic data from rate expressions and for relating the kinetic data to reaction mechanisms [587].

The kinetics of oxidation of L-rhamnose and D-mannose by chromium(VI) in perchloric acid leading to L-1,4-rhamnolactone and D-1,4-rhamnolactone, respectively, was described [588]. The kinetics of oxidation of methanol and ethanol by chromium(VI) in aqueous perchloric acid were studied at 25 °C using spectrophotometric method. The results were exp;ained by a new mechanism which involves an intermediate reaction between chromic acid and perchloric acid [589]. The kinetics of the oxidation of L-ascorbic acid by chromium(VI) have been studied by spectrophotometry in aqueous citrate buffers [590].

The effect of manganese(II) ion on the oxidation of formic acid by chromium(VI) was studied. Inhibition by manganese(II) ion was found only in slightly acid solutions [591].

The kinetics of oxidation of 1,4-butanediol to 4-hydroxybutanal by chromium(VI) was studied in acid perchlorate medium [592]. The kinetics and mechanism of the oxidation of D-mannose to D-arabinose and formic acid with pyridinium chlorochrom-



($R^1$, $R^2$, $R^3$ = Et, H, H; Me, H, H; $Me_2CH$, H, H; H, H, H; Me, H, Me; Me, Me, H.)

**214**

ate were studied in aqueous perchloric acid medium. The acid catalyzed oxidation reaction was found to be first-order in both D-mannose and pyridinium chlorochromate [593]. The oxidation of succinic acid by $CrO_3$ was studied by infrared spectroscopy [594]. The kinetics of oxidation of L-ascorbic acid by chromium(VI) with and without added copper(II) was studied in phosphate buffers [595].

The oxidation of *meso*- and *d,l*-hydrobenzoin by peroxomolybdenum complexes were investigated. When the glycol acts as monodentate ligand, benzil is formed, whereas when it acts as a chelating species, benzaldehyde is the product. Both reactions were found to be homolytic in nature [596].

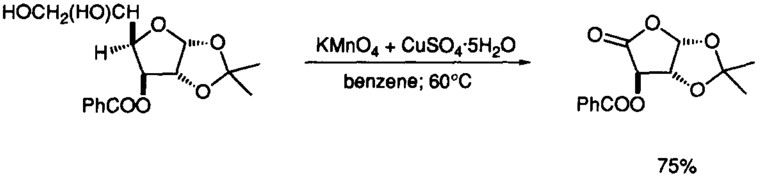
The stoichiometry, kinetics and mechanism of oxidation of *N*-(hydroxyethyl) ethylenediamine triacetate by $K_5Co^{III}W_{12}O_{40}$, $Fe(phen)3^{3+}$, and $Fe(bpy)_3{}^{3+}$ were studied. Each reaction was found to be first-order with respect to the oxidant and the reductant, but retarded by $[H^+]$ in the 0.20–1.60 M range. Carbon dioxide was a major product and in addition glycine, ethylenediamine and formaldehyde were identified by paper electrophoresis [597].

The kinetics and mechanism of oxidation of 4-oxopentanoic acid to acetic acid by aquomanganese(III) ions were investigated [598]. The kinetics of the reaction of manganese(III) with oxalic acid were studied in sulfuric acid solutions [599].

The permanganate ion oxidation of benzaldehyde and substituted benzaldehydes in perchloric acid medium was found to be first-order in $[MnO_4^-]$, but complex-order with respect to [aldehyde] as well as $[H^+]$. A mechanism comprising a fast pre-equilibrium of the aldehyde, $MnO_4^-$ and $H^+$ to form an intermediate permanganate ester, a slow decomposition of the ester to give benzoic acid and manganese(V), and a fast disproportionation of $Mn_V$ to $Mn_{VII}$ and $Mn_{IV}$ was suggested [600]. The kinetics of the oxidation of malonic acid to glyoxylic acid by both permanganate and $MnO_2$ have been studied in a perchloric acid medium [601]. The kinetics of oxidation of 2-propen-1-ol, 2-buten-1-ol, and 3-phenyl-2-propen-1-ol by manganese(III) acetate were studied in aqueous sulfuric acid. The reactions were found to be first-order in $[Mn_{III}]$ and $[H^+]$ and fractional-order in [alcohol]. A mechanism was proposed and activation parameters were evaluated for the 25–40 °C range [602].

The kinetics and mechanism of oxidation of γ-oxoacids, $RC_6H_4C(=O)(CH_2)_2CO_2H$ (R = H, *p*-Ph, *p*-Cl, *p*-Br, *m*-$NO_2$, *p*-Et, *p*-Me, *p*-OMe, *p*-OEt) by permanganate in acetic acid medium were studied. At high $[H_3O^+]$, the reaction was found to be first order each in [oxoacid], $[MnO_4^-]$ and $[H_3O^+]$. The Hammett's plot gave the value of the reaction constant, $\rho = -1.49$ at 30 °C and $[H_3O^+] = 1$ M [603]. The oxidation of pyruvic and lactic acids with permanganate ion in alkaline solution was studied [604]. Manganese(IV) phosphate was found to oxidize oxygen-containing bifunctional substrates in phosphoric acid in an autocatalytic way [605].

The kinetics and mechanism of the oxidation of aliphatic aldehydes to the corresponding carboxylic acids, by bis(2,2′-bipyridyl)copper(II) permanganate were studied. A mechanism involving formation of permanganate ester and its slow decomposition was proposed [606]. Sugars of furanose skeleton having a carbonyl or secondary hydrxyl at C5 were found to be smoothly cleaved at the C4–C5 bond with powdered $KMnO_4/CuSO_4$ reagent in benzene at 60 °C [607]. E.g.:



Rate constants for the oxidation of aliphatic and aromatic acyloins by hexacyanoferrate(III) in 50% aqueous methanol at pH 11.5 were determined. Reaction constants, $\rho = 2.14$ and $\rho^* = 1.3$, for aromatic and aliphatic acyloins, respectively, were obtained [608]. The oxidation of benzoin with $FeCl_3 \cdot 6H_2O$ in acetic acid-water gave 90–95% benzil [609]. The kinetics of oxidation of glycolaldehyde by alkaline hexacyanoferrate(III) were studied [610].

Catalytic amount of polyaniline in combination with stoichiometric amount of copper(II) chloride or iron(III) chloride under dioxygen atmosphere (1 bar) at 80 °C was found to be active in dehydrogenation of cinnamyl alcohol into cinnamaldehyde [611].

The oxidation of lactic acid by Cr(VI) in the presence of sodium lauryl sulfate was found to be first-order in both lactic acid and Cr(VI). The oxidation rate reaches maximum at the critical micelle concentration [612].

The oxidative ability toward the alcoholic function of a series of peroxomolybdenum complexes has been evaluated by measuring the oxidation rates in the oxidation of cyclohexanol and 1-octanol to cyclohexanone and octanal, respectively [613].

The kinetics and mechanism of ruthenium(III) chloride-catalyzed oxidation of butane-1,4-diol to $HO(CH_2)_3CHO$ by thallium(III) in acid perchlorate medium were studied [614]. The kinetics of oxidation of DNA by $Ru(tpy)(L)O^{2+}$ complexes were studied (tpy = 2,2′,2″-terpyridine, L = 2,2′-bipyridine, *o*-phenanthroline, or dihydrophenazine). The cleavage reaction was shown to lead to the release of nucleic acid bases, implicating sugar oxidation as the reaction pathway [615].

The kinetics of oxidation of sodium tartrate by a nickel(IV) periodate complex in aqueous alkaline medium were studied [616]. The kinetics and mechanism of oxidation of tetrahydrofurfuryl alcohol by dihydroxydiperiodatonickelate(IV) complex in the temperature range of 20–35 °C were studied by spectrophotometry in aqueous alkaline medium [617].

The kinetics and mechanism of oxidation of $\alpha,\beta$-unsaturated alcohols, such as allyl, crotyl and propargyl alcohols by diperiodato cuprate(III) in alkaline medium to the corresponding aldehyde was studied spectrophotometrically at 416 nm [618].

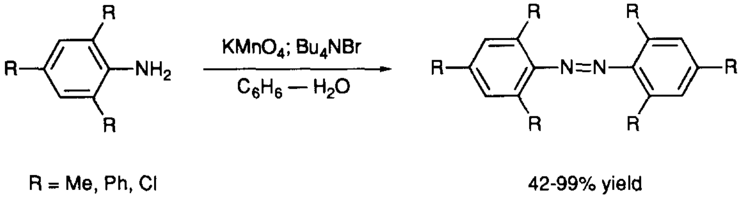
Ascorbic acid in acidic aqueous solution was oxidized by ethylenebis(biguanide)silver(III) via an inner-sphere mechanism to give dehydroascorbic acid, silver(I), and free ethylenebis(biguanide) [619]. The kinetics and mechanism of oxidation of ascorbic acid to dehydroascorbic acid with silver(I) in the presence of pre-added silver(0) were studied in perchloric acid [620]. See also Refs. [551,558,559,564,565].

### *4.6.4. Oxidation of N-containing organic compounds*

The kinetics of oxidation of alanine, leucine, phenylalanine, and valine by quinolinium dichromate in acid medium were studied. The reaction was found to be first-order in substrate, oxidant, and acid. The absence of a kinetic isotope effect was explained that there was no cleavage of the carbon–hydrogen bond in the rate determining step [621]. The oxidative behaviour of glucosamine, galactosamine, and mannosamine towards chromic acid in perchloric acid medium was studied [622]. The kinetics of oxidation of oximes of some piperidin-4-ones and azabicyclic ketones by pyridinium chlorochromate was studied [623].

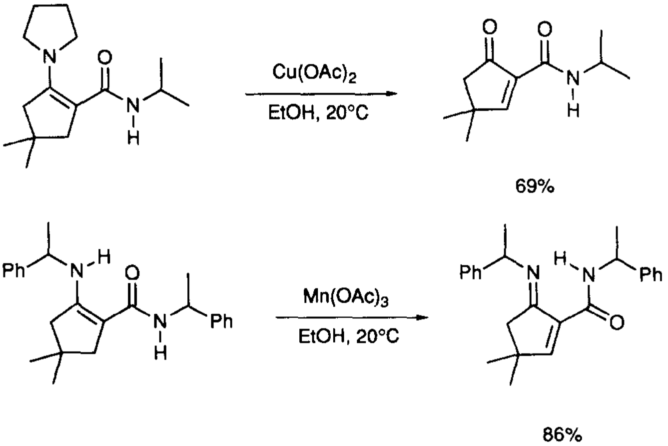
The stoichiometric reactions of $Mo(O)O_2)_2(H_2O)(HMPA)$ with benzylic amines were found to yield the corresponding oximes and/or the Schiff bases. In the presence of hydrogen peroxide as oxidant the oxime formation was found to be catalytic [624].

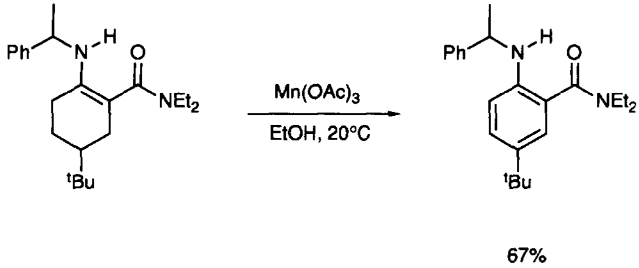
The kinetics of oxidative cleavage of anils of substituted benzaldehydes and benzophenones by manganese(III) acetate to give the corresponding carbonyl compounds in aqueous acetic acid in about 96% yield along with azobenzene in nearly 48% yield were studied [625]. Phase-transfer-assisted permanganate oxidation of primary aromatic amines with optimization of the process conditions permits the selective synthesis of the corresponding diazo compounds [626].



The acid permanganate oxidation of DL-isoleucine was studied by visible spectrophotometry in the presence of sodium dodecyl sulfate at 525 and 420 nm [627]. The kinetics of the autocatalytic oxidation of glycine in buffered acid medium by permanganate were studied [628]. The oxidation of glycine, alanine, and phenylalanine by permanganate under neutral conditions was studied at various temperatures [629].

Dehydrogenation of carboxamidoenamines with manganese(III) acetate or copper(II) acetate gave in a one step procedure α,β-unsaturated imines, ketones or substituted anilines depending on the starting material [630]. E.g.:





A novel stereoselective monoamine oxidase reaction of chiral iron(III) porphyrins and enantiomeric amines was found. Thus, 5,10,15,20-tetrakis[*p*-((−)-menthylcarbamoyl)phenyl]porphyrinato iron(III) chloride or α,α,α,α-isomer of 5,10,15,20-tetrakis [*o*-((*tert*-butyloxycarbamoyl)-L(−)-alaninamino)phenyl] porphyrinato iron(III) chloride and the enantiomeric amines (*R*)-(+)- and (*S*)-(−)-α-phenylethylamine gave at 25 °C in benzene solution under dinitrogen the corresponding iron(II) compound and α-methylbenzylamine. The oxidation of the (*S*)-isomer was found to be up to 1.38 times faster than that of the (*R*)-isomer [631].

The kinetics of oxidation of a series of benzaldoximes to the corresponding benzaldehyde by diperiodatonickelate(IV) was studied in aqueous alkaline medium at different temperatures. First-order dependence on oxidant and substrate, fractional-order dependence on hydroxyl ion and inverse-fractional-order dependence on periodate was found. The order of reactivity was found to be: *p*-OMe > *p*-Me > *p*-Cl > *m*-Cl [632].

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

Potassium oxodiperoxo(pyridine-2-carboxylato)vanadate(V) and potassium oxodiperoxo(3-hydroxypyridine-2-carboxylato)vanadate(V) were found to rapidly oxidize cysteine to cystine in aqueous solution [633].

The Sharpless oxidation (substrate:$Ti(O^iPr)_4$:DIPT:$^tBuOOH$ = 1:1:2:1.1) of some aryl cinnamyl selenides afforded a chiral 1-phenyl-2-propen-1-ol via asymmetric [2,3] sigmatropic rearrangement of the intermediate selenoxides in up to 92% ee [634]. The asymmetric oxidation of $CH_2(SR)_2$ (R = Me, Et), using a modified Sharpless reagent afforded enriched mixtures of sulfoxides (*R*)- and (*S*)-$RSCH_2S(O)R$ [635].

The molybdenum and tungsten peroxofluoro complexes $K_2[MO(O_2)F_4]\cdot H_2O$ (M = Mo, W) were found to oxidize $PPh_3$ to $OPPh_3$ in high yield [636].

In the oxidation reaction of poly(phenylene sulfide) by $KMnO_4$, $H_2O_2$ and concentrated $H_2SO_4$ in aqueous medium the sulfur in the surface layer was oxidized by $KMnO_4$ into $SO_2$. Hydrogen peroxide transformed the sulfur to sulfinyl or sulfonyl groups depending on the applied molar ratio and reaction time [637].

The kinetics of the permanganate oxidation of P(III) compounds (phosphorous acid, mono- and diethyl phosphonate and their anions) were investigated. Results indicate that attack of the oxidant on the P–H bond is rate-determining for all substrates in both acidic and basic solutions [638].

The kinetics of oxidation of 1,1′-bis(methoxycarbonyl)ferrocene by hexakis(*N*,*N*-

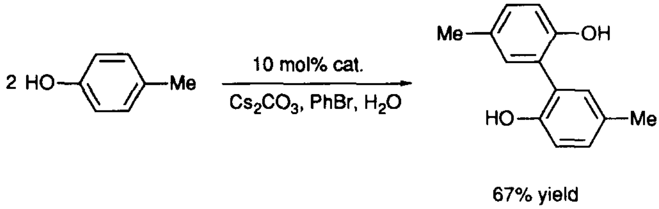
dimethylformamide)iron(III) perchlorate were studied in acetonitrile at 25 °C [639]. The kinetics of oxidation of glutathione by diaquatetrakis(2,2′-bipyridine)-$\mu$-oxo diruthenium(III) ion in aqueous $HClO_4$ have been investigated. The reaction is first order in both oxidant and reductant and negative first order in $[H^+]$ [640]. The kinetics and mechanism of the oxidation of thioanisoles and methyl phenyl sulfoxides by oxo(phosphine)ruthenium(IV) complexes were studied. The substrate oxidations are first-order in substrate concentration and first-order in ruthenium concentration. Based on kinetic isotope effects and Hammett-type analyses of the kinetics a single-electron transfer as the rate-determining step in the oxidation of thioanisole by $[Ru(bpy)_2(O)PPh_3][ClO_4]$ was suggested. The rate-determining step of the oxidation of methyl phenyl sulfoxide involves an $S_N2$ mechanism [641]. See also Ref. [558].

### 4.6.6. *Oxidative coupling reactions*

Oxidation of **215** with $VO(OEt)Cl_2$ in dichloromethane gave **216** in 54% yield [642].

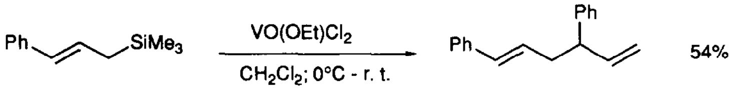
The oxidative coupling of **217** using $VOF_3/BF_3 \cdot OEt_2$ as the oxidant afforded **218** in 81% yield. The use of $Mn(acac)_3$ in place of $VOF_3$ provided **218** in only 42% yield [643].

($\eta^6$-Benzene)($\eta^5$-ethyltetramethylcyclopentadienyl)rhodium(III) hexafluoro-phosphate was found to be a useful reagent for catalytic phenol oxidative coupling [644]. E.g.:

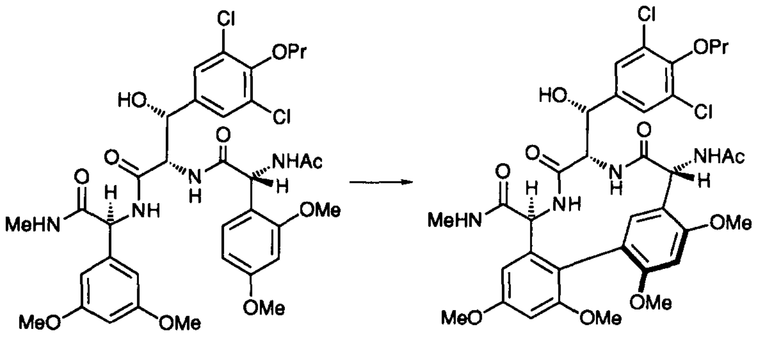


The oxidative coupling of benzene to biphenyl was achieved by the palladium(II) acetate-dialkyl sulfide system at 70 °C [645]. Biaryl **219** was obtained with 50–85% selectivity in the oxidative cross-coupling reaction of *p*-methoxyphenol and *p*-cresol with $FeCl_3$, $VOCl_3$ and $CuBr_2$ in the presence of $AlCl_3$ at 25 °C in nitromethane [646].

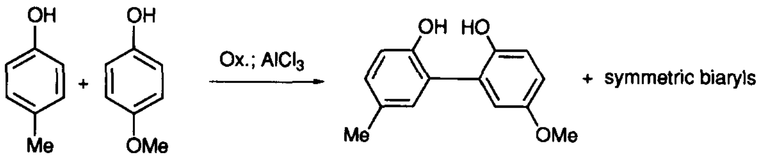
The in situ generated complexes of $CuCl_2$ and chiral amines, sparteine or $PhCH(NH_2)Me$, were utilized to synthesize enantiomerically enriched biaryl derivatives **220–223** and **224** by oxidatively coupling the corresponding precursors at room temperature. Up to 100% ee was observed [647].



**215** **216**



**217** **218**



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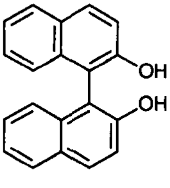

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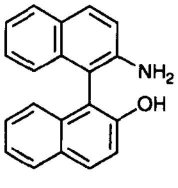

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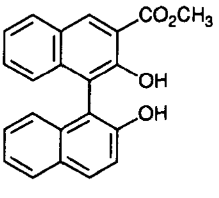

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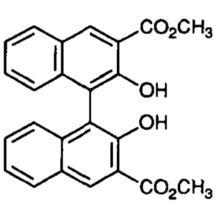

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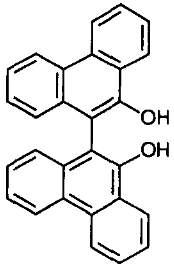
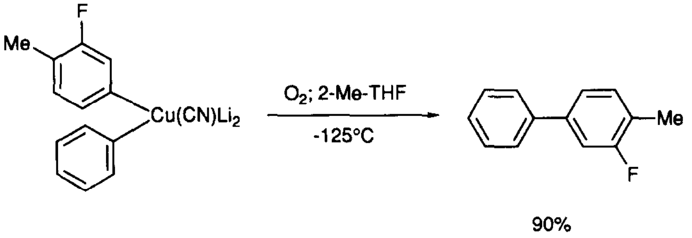
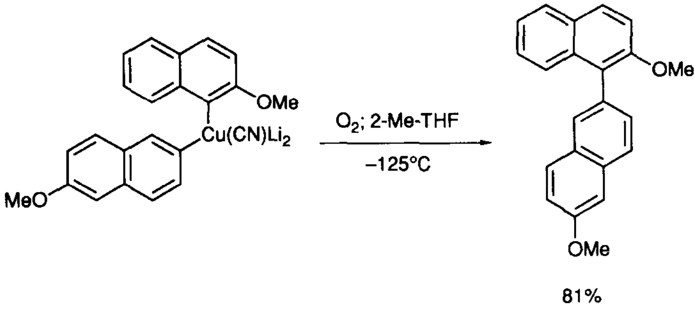


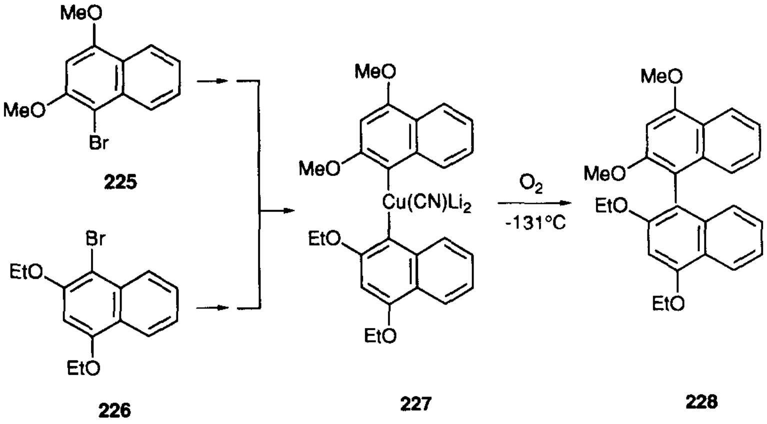
**224**

Exposure of kinetically generated higher order arylcyanocuprates Ar(Ar′)Cu(CN)$Li_2$, prepared from ArCu(CN)Li and Ar′Li, to ground-state dioxygen at −125 °C in 2-methyl-THF afforded good yields of the unsymmetrical biaryl Ar–Ar′ [648]. E.g.:

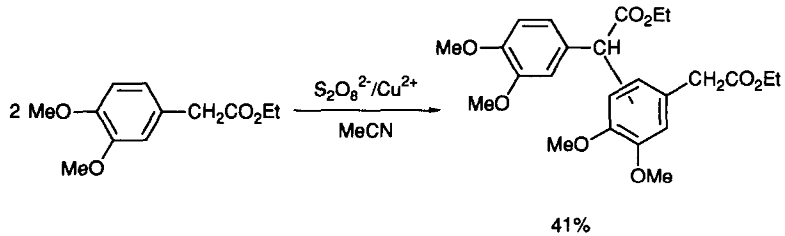




Oxidation of the cyanocuprate intermediate **227** by dioxygen at −131 °C the cross-coupling product **228** was obtained in 67% isolated yield based on the starting naphthalene derivatives **225** and **226** [649].



The oxidative coupling of various benzylic compound by $S_2O_8^{2-}/Cu^{2+}$ was studied [650]. E.g.:



The oxidation of *p*-methoxyphenylacetone by $S_2O_8^{2-}/Cu^{2+}$ in refluxing acetonitrile afforded two isomeric oxazoles **229** and **230** as well as a coupled dimer **231** [651].

### 4.6.7. *Electrooxidation and photooxidation*

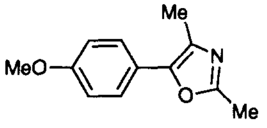
The oxidation of alkanes and benzene by $VO(O_2)$(2-picolinate)·$2H_2O$ in acetonitrile media was found to be accelerated under irradiation with visible and especially UV-light. Cyclohexane is transformed both in the dark and under irradiation into cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone in a ratio ca. 2:1:1. Benzene is oxidized to afford phenol [652].

The electrooxidation of naphthalene and 2-methylnaphthalene to the corresponding 1,4-naphthoquinone was found to be enhanced by dichromate ion. An improvement of the selectivity (>60%) was achieved using $RuCl_3 \cdot 3H_2O$) as the co-catalyst [653]. Electrochemically generated $M_6X_{14}^-$ ions (M = Mo, W; X = Cl, Br, I) were found to oxidize benzyl alcohol to benzaldehyde [654].

Electroassisted oxidation of hydrocarbons such as tetraline, cyclohexane, cyclooctane, cyclooctene, and adamantane by molecular oxygen catalyzed by manganese porphyrin complexes intercalated into montmorillonite has been studied [655].

The ferric chloride-catalyzed photooxygenation of cyclohexane with air in isopropanol or methanol gave cyclohexanol and cyclohexanone [656].

The ruthenium(V)-oxo complex $[Ru^V(O)(H_2O)_3Cl_2](PF_6)$ was used as an electrocatalyst for the oxidation of olefinic substrates to epoxides and $PPh_3$ to



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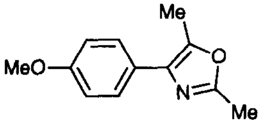
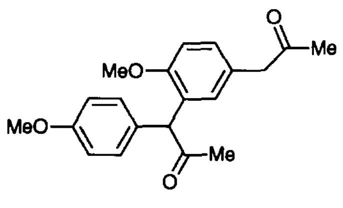


**230**



**231**

triphenylphosphine oxide [657]. *Cis*-$[Ru^V(L)(Cl)(O)]^{2+}$ (L = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)ethylenediamine) was found to be an active catalyst for the electrooxidation of methanol in solution [658].

The asymmetric synthesis of (*R*)-(+)-1,1′-bi-2-naphthol (16.2% ee) (or (*R*)-(+)-1,1′-bi-3-methoxy-2-naphthol (4% ee)) from 2-naphthol (or 3-methoxy-2-naphthol) was performed photocatalytically by using a chiral ruthenium complex as a photosensitizer and cobalt(III) acetylacetonate as an oxidant [659].

The electrocatalytic oxidation of styrene with dioxygen in the presence of copper(II) chloride in acetonitrile gave benzaldehyde [660]. Electrocatalytic oxidation of dimethylphenylsilane in the presence of $CuCl_2$ or CuCl afforded chlorodimethylphenylsilane in >90% yields. In the presence of $BF_4^-$ ions, the electrolysis afforded fluorodimethylphenylsilane in 90% yield [661].

The validity of the geminate-pair scavenging mechanism in the photooxidation of organic substrates in the presence of chlorocopper(II) complexes was studied [662].

## 5. Reviews

Catalysis of the water gas shift reaction. 82 Refs. [663].

An in-situ infrared study of carbon dioxide reduction catalyzed by rhenium tricarbonyl bipyridyl derivatives. A review with commentary and 11 Refs. [664].

Mechanistic aspects of metal complex-catalyzed alternating copolymerization of olefins with carbon monoxide. More than 31 Refs. [665].

A review of hydrogenation, hydrocyanation, hydroformylation, and the Wacker-process with water-soluble catalysts [666].

Chiral semicorrins and related nitrogen heterocycles as ligands in asymmetric catalysis. More than 45 Refs. [667].

Electronic effects on the synthesis, structure, reactivity, and selectivity of rhodium hydroformylation catalysts. 38 Refs. [668].

Supported aqueous-phase catalysis. A review with 27 Refs. with emphasis on the hydroformylation rection [669].

Asymmetric hydrogenation with ruthenium-BINAP catalyst. 10 Refs. [670].

Practical ruthenium catalysts for asymmetric syntheses. A review with 7 Refs. on asymmetric hydrogenation of olefins and ketones with ruthenium complex catalysts containing BINAP as ligand [671].

Enantioselective transition metal-catalyzed hydrogenation in asymmetric amine synthesis. More than 15 Refs. [672].

Ruthenium-catalyzed hydrogen transfer reactions and their application to oxidation of alcohols and reduction of ketones and imines. More than 40 Refs. [673].

Stereoselectivity. The ultimate challenge in catalysis. A review with 16 Refs. on asymmetric catalysis beginning with the work of W.S. Knowles et al. (1968) [674].

*Para*-hydrogen-induced polarization and polarization transfer in hydrogenation and oxidative addition reactions. A mechanistic probe 46 Refs. [675].

Hydroformylation and hydrogenation with platinum phosphinito complexes. 33 Refs. [676].

Oxides as heterogeneous promoters for liquid-phase hydrocarbonylation reactions with iodocarbonylruthenium catalysts. 26 Refs. [677].

Influence of organophosphines on the hydroformylation of olefins catalyzed by anionic ruthenium clusters. 12 Refs. [678].

Amidocarbonylation. Catalysts, reaction scope, and industrial application. 20 Refs. [679].

The catalytic activities of rhodium and rhodium-cobalt mixed metal complexes in hydrosilylation, silylformylation, and novel silylcarbocyclization reactions were reviewed with 24 Refs. [680].

Catalytic asymmetric synthesis of optically active 2-alkanols and cyclic alcohols via hydrosilylation of 1-alkenes and cyclic olefins with a chiral monophosphine-palladium catalyst. A review with commentary and 6 Refs. [681].

Recent advances in catalytic hydrosilylation. A short review dealing with reports published in the last two years concerning catalytic, mechanistic, synthetic and structural aspects of hydrosilylation as well as asymmetric syntheses involving hydrosilylation. 111 Refs. [682].

Catalyzed and noncatalyzed hydrosilylation of organotransition metal acyl complexes. 17 Refs. [683].

Addition reactions of Ge–H functional organogermanes $R_nGeH_{4-n}$ ($R=$alkyl and/or aryl; $n=1, 2, 3$) to alkenes, alkynes, ketones, aldehydes, etc. were reviewed. More than 164 Refs. [684].

Enantioselective hydroboration of alkenes with catecholborane in the presence of optically active rhodium complexes has been reviewed. 43 Refs. [685].

Asymmetric epoxidation using chiral manganese(III)–salen complexes. A review with 21 Refs. [686].

Activation of alkanes: the biomimetic approach. A review with 23 Refs. [687].

A new step in asymmetric oxidation reaction. A review with 10 Refs. on recent advances of asymmetric dihydroxylation and asymmetric epoxidation of olefins in the presence of $OsO_4$-chiral ligand, and Mn(III)-salen complexes, respectively [688].

Homogeneous and heterogeneous catalytic oxidations with peroxide reagents. 43 Refs. [689].

Oxidation of several organic substrates by dodecatungstocobaltate(III). 12 Refs. [690].

Epoxidation and hydroxylation. A review with more than 382 Refs. [691].

The use of hypochlorites for oxidations at saturated or unsaturated carbons and heteroatoms and oxidative cleavage of carbon–carbon bonds. 104 Refs. [692].

Biomimetics for cytochrome P 450 and oxidative enzyme model in asymmetric oxidation. 14 Refs. [693].

Enantioselective *cis*-hydroxylation. A review describing the versatility of $OsO_4$-mediated enantioselective *cis*-hydroxylation of olefinic double bonds using chiral N bases as the ligands of osmium. 39 Refs. [694].

Application of pyridinium chlorochromate in selective oxidation. 26 Refs. [695].

New mechanistic insights into reductions of halides and radicals with samarium(II) iodide. 69 Refs. [696].

Beyond nature's chiral pool: enantioselective catalysis in industry. 40 Refs. [697].

Transition-metal-catalyzed oxidation. Synthetic applications and the role of peroxometal complexes. 149 Refs. [698].

Selectivity and mechanism in catalytic asymmetric synthesis. 34 Refs. [699].

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Oxidation of organic substrates by potassium hexacyanoferrate(III) 108 Refs. [701].

Macrocyclic nickel complexes in DNA recognition and oxidation. 28 Refs. [702].

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Chemical catalysis by colloids and clusters. 402 Refs. [704].

Asymmetric dihydroxylation of olefins catalyzed by osmium tetroxide. 22 Refs. [705].

Regioselective and enantioselective epoxidation catalyzed by metalloporphyrins. 41 Refs. [706].

Enantioselective epoxidation with proxidic oxygen. 25 Refs. [707].

Catalytic oxidations with hydrogen peroxide as oxidant. Nucleophilic and electrophilic catalysis with transition metal complexes. A review with ca. 195 Refs. [708].

## 6. List of abbreviations

| | |
|---|---|
| acac | acetylacetonate |
| BDPP | 2,4-bis(diphenylphosphino)pentane |
| BINAP | 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl |
| Bn | benzyl |
| bppm | see Fig. 68 |
| BPE | see Fig. 52 |
| bpy | 2,2′-bipyridine |
| Bz | benzoyl |
| CAN | ceric ammonium nitrate |
| $^c$Hex | yclohexyl |
| CHIRAPHOS | 2,3-bis(diphenylphosphino)butane |
| $Cl_8$TPP | itmeso-tetrakis(2,6-dichlorophenyl)porphinato |
| COD | 1,5-cyclooctadiene |
| Cp | cyclopentadienyl, $\eta5$-$C_5H_5$ |
| Cp* | pentamethylcyclopentadienyl, $\eta^5$-$C_5Me_5$ |
| dba | dibenzylideneacetone |
| DET | diethyl tartrate |
| DIOP | see Fig. 69 |
| DMF | *N*,*N*-dimethylformamide |
| DIPAMP | 2,4-bis(2-methoxyphenyl, phenyl)butane |
| DIPT | diisopropyl tartrate |
| dppe | 1,2-bis(diphenylphosphino)ethane |
| dppb | 1,4-bis(diphenylphosphino)butane |

| | |
|---|---|
| dppp | 1,3-bis(diphenylphosphino)propane |
| DuPHOS | see Fig. 53 |
| ee | enantiomeric excess |
| Hdmg | dimethylglyoxime |
| HMPA | hexamethylphosphoric acid triamide |
| NBD | norbornadiene |
| NORPHOS | 2,3-bis(diphenylphosphino)bicyclo[2.2.1]hex-5-ene |
| NMO | *N*-methylmorpholine-*N*-oxide |
| phen | 1,10-phenanthroline |
| PROPHOS | (*R*)-1,2-bis(diphenylphosphino)propane |
| py | pyridine |
| r.t. | room temperature |
| salen | *N*,*N*′-bis(salicylidene)-ethylenediaminato |
| TBHP | *tert*-butyl hydroperoxide |
| Tf | triflate |
| TPP | *meso*-tetraphenylporphinato |
| Ts | *p*-toluenesulfonyl |

## 7. Metal index

| | |
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| Ag | 376, 524, 619, 620 |
| Au | 51, 189 |
| Zn | 43, 339, 350 |
| Hg | 376 |

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