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Transition metals in organic synthesis: hydroformylation, reduction, and oxidation. Annual Survey covering the year 1991 *

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Contents

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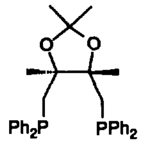
1. Theoretical calculations

The insertion of Fe, Co, Ni, Rh, and Pd atoms into the C–C and C–H bonds was studied using quantum chemical methods including electron correlation. The barrier for C–C insertion was found to be 14–20 kcal mol^{-1} higher than the barrier for C–H insertion [1]. The importance of steric factors in determining the regioselectivity of $L_2Pt(CO)X$-type hydroformylation catalysts was theoretically examined by using an augmented Dreiding force field (L_2 = (–)-DIOP, **1**; (–)-BPPM, **2**; (–)-DBP-BPPM, **3**; and DPC, **4**). The factors favoring primary *vs.* secondary alkyl intermediate formation, resulting from pentene and styrene insertion into a Pt–H bond, were investigated [2].



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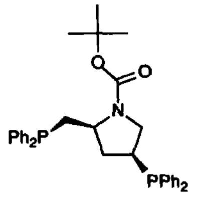

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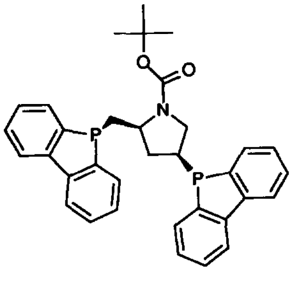

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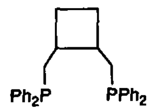


4

The reductive elimination reaction of $RCOCo(H_2)(CO)_3$ — in connection with the cobalt-catalyzed olefin hydroformylation — was studied by the atom superposition and electron delocalization MO method [3].

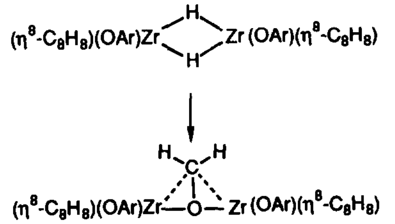
The IEHMO method was used to study the interaction of ethylene with $[MO_2(O)_2]^{2-}$ and $[MO_3(O)_2]^{2-}$ (M = Mo, W) in connection with the mechanism of epoxidation [4]. The configuration of $[PdCl_2(C_2H_4OH)]^-$ was studied by the pseudopotential *ab initio* method. A *cis* isomer was found to be the reaction intermediate in the Wacker process [5]. A mechanistic study of the epoxidation of allylic alcohols catalyzed by titanium-tartrate complexes and the *cis*-dihydroxylation of alkenes by OsO_4 and OsO_4-chiral diamine ligand complexes was published. The structure of the titanium-tartrate complexes and the oxygen transfer were discussed on the basis of the frontier-orbital approach [6].

2. Hydroformylation and related reactions of CO

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

The chemistry of $IrCl(CO)_3$ and $Ir_4(CO)_{12}$ in a $AlCl_3 \cdot NaCl$ melt has been studied *in situ* spectroscopically during catalytic hydrogenation of CO. It was shown that similar monomeric species are generated from both precursors during catalysis [7]. The catalytic activity of $(\mu\text{-}Ph_2P)(\mu\text{-}{}^tBuS)Fe_2(CO)_6$ in the reduction of CO has been tested [8].

The dimeric hydrido complex **5** reacts with 1 bar CO at room temperature in toluene solution to afford the dimeric formaldehyde complex **6** [9].



5

6

Ru–Co bimetallic carbonyl clusters deposited on silica were used as catalysts in CO hydrogenation. C_1–C_5 alcohols (mainly n-alcohols) were produced along with C_1–C_5 hydrocarbons [10]. Several Ru and Rh catalysts were described and discussed with respect to ligands and increased selectivity in ethylene glycol manufacturing from synthesis gas in one step [11].

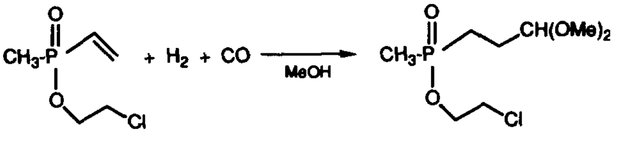
2.2. Hydroformylation

2.2.1. Cobalt catalysts

The cobalt-catalyzed hydroformylation of propene in supercritical carbon dioxide as the medium has been studied by means of high-pressure NMR spectroscopy. The rate of aldehyde formation and the steady-state concentrations of the catalytic intermediates ($C_3H_7COCo(CO)_4$, $HCo(CO)_4$, and $Co_2(CO)_8$) were found to be comparable to values for other linear-terminal olefins in saturated hydrocarbon solvents. The aldehyde product consists of 88% n-butyraldehyde [12].

The effect of pyridine on cobalt carbonyl catalysts employed in hydroformylation, hydrocarboxylation, and hydroalkoxycarbonylation was studied by Raman and IR spectroscopy. The presence of $[pyH]^+[Co(CO)_4]^-$ ion pairs was confirmed [13].

Hydroformylation of 1-hexene under two-phase and supported aqueous phase reaction conditions using $Co_2(CO)_6(P(m\text{-}C_6H_4SO_3Na)_3)_2$ as the catalyst precursor has been reported [14]. Hydroformylation of **7** at 120°C and 100 bar $CO/H_2 = 1$ in methanol gave **8** in 90% yield [15].



7 **8**

The mechanism of formation of isomeric aldehydes in the cobalt-catalyzed hydroformylation was studied by analyzing of the products of deuteroformylation of propene and hydroformylation of deuteropropenes, together with revised data for the hydroformylation of but-1-ene-4-d_3. It was concluded that several reaction paths account for the products depending on the reaction conditions and the structure of the substrate [16]. The catalytic pathways in the cobalt- and rhodium-catalyzed deuteroformylation of styrene were deduced from ^2H NMR analysis of the crude reaction mixtures after partial substrate conversion [17].

The cobalt-catalyzed hydroformylation of hexenes was found to proceed even at ambient temperature under UV irradiation in the presence of PBu_3. The effect of CO partial pressure and PBu_3 was studied. The photochemical hydroformylation yielded a straight-chain product to branched products ratio of about 10:1 [18]. Low molecular weight commercial polyisobutene (MW = 442) was hydroformylated at 190 bar and 155°C in benzene solution using PPh_3-modified cobalt catalyst [19]. Hydroformylation of N-alkenylamides and α-alkenyllactames catalyzed by $Co_2(CO)_8$, $Co_2Rh_2(CO)_{12}$, and $RhCl(PPh_3)_3$ was reported [20]. Monoformyltricyclodecenes, diformyltricyclodecanes and di(tricyclodecenyl)ketones were obtained in hydroformylation and hydrocarbonylation of *endo*-dicyclopentadiene using $Co_2(CO)_8 + Rh_4(CO)_{12} + PPh_3$ as the catalytic system depending on the reaction conditions [21]. The influences of temperature, pressure, and solvents on the hydroformylation of some olefins using a heteronuclear metal cluster $[PhCH_2NMe_3][RuCo_3(CO)_{12}]$ as the catalyst precursor was studied [22]. Rate constants for the hydroformylation of 1-hexene in MeCN using $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, or $Co_2Rh_2(CO)_{12}$ as catalyst precursors were determined at various temperatures and synthesis gas pressures [23].

2.2.2. Rhodium catalysts

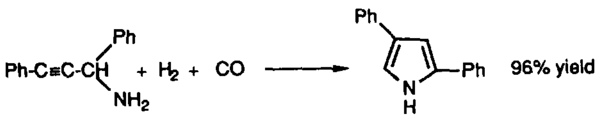
Deuteroformylation of styrene using $Rh_4(CO)_{12}$ as catalyst precursor was investigated between 25 and 130°C and 180 bar $D_2/CO = 1/1$ pressure. At room temperature, only the two aldehydes expected on a stoichiometric basis were formed and neither HD nor labeled styrenes were found. At higher temperature, variable deuterium incorporation occurred in the reactants and in the products [24]. The hydroformylation of cyclooctene at 60°C and 20 bar H_2/CO (or D_2/CO) in the presence of rhodium tri(*o*-t-butylphenyl)phosphite complexes as catalyst was investigated. Isotope studies supported by *in situ* high-pressure NMR and IR spectra indicated that the aldehyde-forming step is a direct reaction of the rhodium acyl complex with dihydrogen (dideuterium) [25].

The results of high-pressure spectroscopic studies of reactions of the clusters $[Rh_4(CO)_{12-x}\{P(OPh)_3\}_x]$ (x = 1–4) with CO or syngas were discussed in light of hydroformylation catalysis for olefins [26]. The reaction mixture of hydroformylation with $HRh(CO)(PPh_3)_3$ catalyst was investigated *in situ* by ^1H NMR spectroscopy under industrial conditions (10 bar $H_2 + CO$, 70°C). The ^1H signal of a rhodium carbonyl hydride complex was observed [27].

The deactivation mechanism of PPh_3 modified rhodium cluster catalysts for the hydroformylation of olefins at 50°C and 1 bar was investigated by IR spectroscopy and HPLC. The active complexes were identified as $Rh_2(CO)_4(PPh_3)_4$ and $Rh_2(CO)_6(PPh_3)_2$. Decay of catalyst activity was attributed to the instability of the active species [28]. It was found that deactivation of rhodium carbonyl hydroformylation catalysts containing the $(PhO)_3P$ ligand occurs by formation of a complex containing a $(PhO)_2POH$ ligand. Using excess olefin (2-butenes) can suppress the catalyst deactivation during hydroformylation [29]. The effect of temperature, PPh_3 concentration, and solvents on the deactivation of $HRh(CO)(PPh_3)_3$ catalyst in the hydroformylation of 1-hexene was investigated [30].

The kinetics of vinyl acetate hydroformylation using $[Rh(CO)_2Cl]_2$ as the catalyst were investigated at 80°C. The rate dependence was found to be fractional order in the catalyst concentration and first order in both dihydrogen and carbon monoxide partial pressure. The dependence of the rate on vinyl acetate concentration passed through a maximum and showed substrate-inhibited kinetics at higher concentrations [31]. The rate equation of ethene hydroformylation with a Rh–PPh_3 complex catalyst in propionaldehyde as the solvent was determined. Fractional orders were obtained for all reactants and the rate showed a maximum with CO partial pressure [32].

Hydroformylation of 2-vinylfuran using Rh(acac)-$(CO)_2$ as the catalyst gave α- and β-(2-furyl)propionaldehyde in a ratio 81 : 19 with 96% overall yield. The selectivity of branched chain aldehyde formation could be increased to 94% by the addition of $P(OPh)_3$ (P : Rh = 9 : 1) [33]. Rh(AA)$(CO)_2$ (HAA = anthranilic acid) was used as a catalyst precursor in olefin hydroformylation [34]. Camphene was hydroformylated at 100°C and 100 bar CO + H_2 using Rh–phosphine catalyst systems formed *in situ* from $[Rh(COD)Cl]_2$ and different monodentate or bidentate phosphines. Ligands with large cone angles like P(*o*-tolyl)$_3$ gave mainly *exo* aldehydes; bidentate ligands with smaller cone angles provided catalyst systems with only low activity because of the tendency to form phosphine-bridged dinuclear Rh carbonyls [35]. Mono- and dinuclear rhodium complexes containing 2-(diphenylphosphino) pyridine as ligand have been examined as catalysts for the hydroformylation of styrene, 1-octene, and cyclohexene [36]. The dinuclear rhodium complexes $[Rh_2(\mu\text{-}SR_2)_2(CO)_2L_2]$, where L = PPh_3, $P(OPh)_3$, or $P(OMe)_3$, were found to be efficient catalyst precursors for the selective hydroformylation of limonene, isopulegol, isopulegyl acetate, α- and β-pinene at 5–17 bar $CO/H_2 = 1/1$ and 85°C [37]. The complexes $[Rh_2(\mu\text{-}S(CH_2)_3NMe_2CH_2Ph)_2L](PF_6)_2$ (L = $(COD)_2$ or $(CO)_4$) catalyze the hydroformylation of 1-heptene at 80°C and 5 bar $CO/H_2 = 1/1$ in the presence of PPh_3, $P(OPh)_3$, or $P(OMe)_3$ ligands as cocatalysts [38]. Substituted pyrroles such as **9** were prepared in good yields by $[Rh(OAc)_2]_2$ + PPh_3-catalyzed hydroformylation of β-alkynylamines at 70°C and 28 bar CO : H_2 = 1 : 1 [39].



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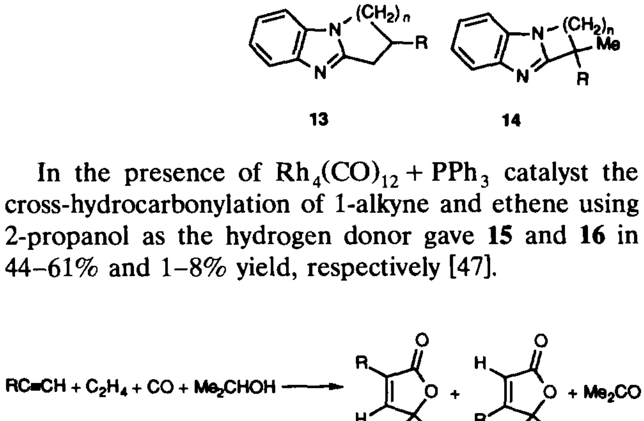
An extremely fast hydroformylation of 1-octene was achieved, with a 2 : 1 linear to branched ratio of aldehyde product, using $Rh(CO)_2$(2,4-pentanedionate) as catalyst precursor in the presence of a hundredfold excess of tris(*o*-t-butyl-*p*-methylphenyl)phosphite at 70–80°C [40]. Enhancement in rate and selectivity in hydroformylation of allyl alcohol using HRh(CO)-$(PPh_3)_3$ as catalyst and higher linear alcohols as solvent was reported. The rate and the normal/iso ratio increased from 1.7 when ethanol was used as solvent, to 15 when octanol was used [41].

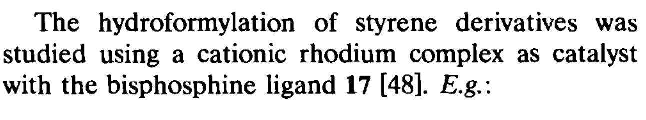
Up to 55% yield of ethyl 2-formylpropanoate was obtained in the regioselective hydroformylation of ethyl acrylate using *in situ* generated catalysts from $[Rh(CO)_2Cl]_2$ and phospholes or phosphanorbornadienes [42]. The hydroformylation of 2-butenes in the presence of rhodium carbonyl catalysts modified with organophosphorus ligands was studied [43].

Hydroformylation of commercial methyl oleate (20% methyl linoleate content) at 140°C and 300 bar in the presence of a copolymer of $Ph_2P(CH_2)_3Si(OEt)_3$ with $RhCl_3(MeCN)_3$ gave a mixture which contained 97% monoformylated and 2% diformylated product [44]. Good to excellent regiocontrol was obtained for the internal product of rhodium-catalyzed hydroformylation of a range of alkenylphosphines. Thus, hydroformylation of $CH_2{=}CHCH_2CH_2PPh_2$ in the presence of $Rh_2(OAc)_4$ gave 100% $HOCH_2CH(Me)CH_2CH_2$-PPh_2 [45].

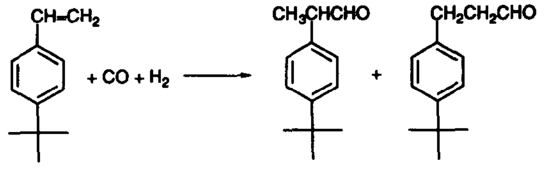
Rhodium-catalyzed ($[Rh(OAc)_2]_2$ + PPh_3) reactions of **10** with H_2 and CO (28 bar) at 70°C gave *via* the corresponding aldehydes **11** and **12** benzimidazoles **13** and **14**, respectively, in excellent yields [46].

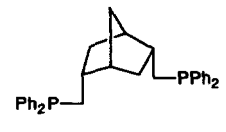


In the presence of $Rh_4(CO)_{12}$ + PPh_3 catalyst the cross-hydrocarbonylation of 1-alkyne and ethene using 2-propanol as the hydrogen donor gave **15** and **16** in 44–61% and 1–8% yield, respectively [47].



The hydroformylation of styrene derivatives was studied using a cationic rhodium complex as catalyst with the bisphosphine ligand **17** [48]. *E.g.*:





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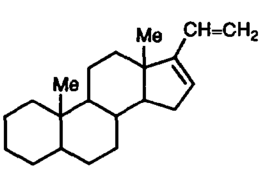
Hydroformylation of vinylandrostene (**18**) with Rh and Pt catalysts afforded a variety of identified aldehydes and hydrogenation products [49].

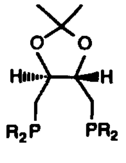


18

The asymmetric hydroformylation of **19** was efficiently catalyzed by $HRh(CO)(PPh_3)_3$ in the presence of (−)-DIOP and related chiral chelating diphosphines. Preferential insertion of CO always occurred onto the *re* face of the substrate giving the (*R*)-antipodes of **20** in up to 60% ee [50]. Very low enantioselectivities (0.1–5.1% ee) in rhodium- and platinum-catalyzed hydroformylation of various olefins have been found by using chiral fully alkylated diphosphines **21** and **22** as ligands [51].

19 **20**

R = Ac, R' = Me, CH$_2$Ph
R = *t*-BuO$_2$C, R' = Me

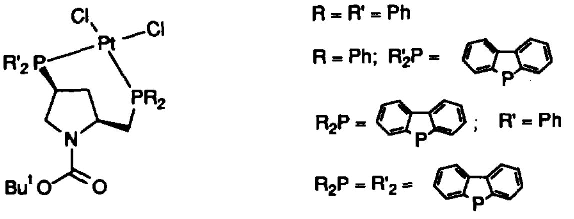


21 R = Et
22 R = *c*-Hx

Heptyl to heptadecyl aldehydes were prepared in > 90% selectivity and conversion of olefins in a two-phase system with $RhCl_3 \cdot H_2O + P(m\text{-}C_6H_4SO_3Na)_3 + H_2O + EtOH$ as catalyst. The addition of EtOH increased the catalytic activity [52]. The hydroformylation of 1-tetradecene in an aqueous-organic two-phase system by means of a water-soluble catalyst containing of $Rh_4(CO)_{12}$ and sulfobetaine derivatives of tris(2-pyridyl)phosphine was investigated [53]. The hydroformylation of 1-hexene in the presence of $HRh(CO)[PPh_2(3\text{-}C_6H_4SO_3Na)]_3$ gave lower yields of products when α-cyclodextrin is added to the biphasic reaction system; a reaction between cyclodextrin and the catalyst was implied [54]. See also [17,20,21,23].

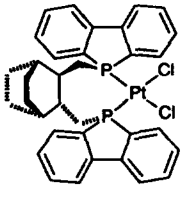
2.2.3. Platinum catalysts

The catalytic activity of some of $MM'(\mu\text{-}X)(\mu\text{-}X')Z_2L_2$ (M = M' = Pt or Pd; M = Pt, M' = Pd; X = X' = Cl, SR'; X = Cl, X' = SR'; Z = Cl, $SnCl_3$, R; L = tertiary phosphine) complexes in the presence of $SnCl_2 \cdot 2H_2O$ as co-catalyst in homogeneous hydrogenation and hydroformylation were described [55]. Various olefins were hydroformylated at 100°C and 100 bar $CO/H_2 = 1$ in the presence of methanesulfonic acid and $Pt(C_2H_4)(DPPB)$ as catalyst (DPPB = 1,4-bis(diphenylphosphino)butane). The regioselectivity towards the formation of linear aldehydes is comparable with that obtained with $[PtCl_2(diphosphine)] + SnCl_2$ as catalyst [56]. Hydroformylation of linear butenes with the $PtCl_2(COD) + SnCl_2 + P(OPh)_3$ catalytic system was investigated. Selective hydroformylation of *Z*-2-butene to 2-methylbutanal and of 1-butene to n-pentanal was achieved by modification of the catalyst by (PPN)Cl [57]. Three steps involved in the hydroformylation of 1-pentene (insertion of the olefin, insertion of carbon monoxide, and hydrogenolysis) by platinum–tin systems were investigated in stoichiometric model reactions. The intermediate hydrido, alkyl, and acyl complexes were prepared and characterized [58]. In the platinum-catalyzed asymmetric hydroformylation of vinyl aromatic compounds with **23** + $SnCl_2$-based catalyst systems the branched aldehydes were formed with complete enantioselectivity (> 96% ee), when the reactions were carried out in the presence of triethyl orthoformate at 60°C and 166 bar $CO/H_2 = 1/1$ [59].



23

Using **24** + $SnCl_2$-based catalyst systems for the enantioselective hydroformylations of styrene and of 1-butene, 86.3% and 67% optical yields were reported, respectively. The enantioselectivity in this case was not improved by carrying out the reaction in the presence of triethyl orthoformate. Other platinum complexes as catalyst precursors such as **25**, **26**, and **27** gave lower optical yields [60].



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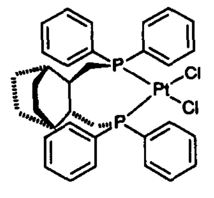

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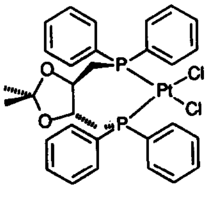

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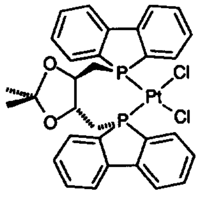

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The strong temperature dependence of the absolute configuration of the α-phenylpropanal formed in the $PtCl_2$[(*S*)-BINAP]-catalyzed hydroformylation of styrene has been explained based on a dynamic NMR study by the restricted rotation of the phenyl rings [61]. See also [49,51].

2.2.4. Other metals as catalysts

Sulfided Ni, Co, Fe, Ru, Ir, and Os catalysts show hydroformylating activity for ethene at 150–300°C and 10 bar [62]. Propene and ethene were hydroformylated using the water-soluble triruthenium cluster, $Ru_3(CO)_9(Ph_2P\text{-}m\text{-}C_6H_4SO_3Na)_3$, as catalyst at 80–120°C and 27–50 bar. From propene n-butyraldehyde was formed as the main product (n/i butyraldehyde ratio 15.9), in the case of ethene besides propionaldehyde diethyl ketone and pentanol-3 were also formed as byproducts [63]. The complex, $[RuH(CO)(NCMe)_2(PPh_3)_3][BF_4]$, was used in catalytic hydroformylation of 1-hexene. At 150°C and 100 bar $CO/H_2 = 2/1$ in toluene solution 30% hydrocarbons (hexane and 2-hexenes), 10% aldehydes and 60% alcohols (n/i = 0.9) were formed. The recovered Ru complex was $[RuH(CO)_3(PPh_3)_2][BF_4]$ [64]. Selective hydroformylation of 1-octene was found by using $Ru_2(\mu\text{-}OAc)_2(CO)_4(PPh_3)_2$ as catalyst precursor and a slight excess of PPh_3 at 80°C and 30 bar $CO/H_2 = 1/1$ [65]. Cycloalkanemethanols were synthesized in 15–86% yields in a one-pot reaction *via* hydroformylation of the corresponding cycloalkenes in the presence of aqueous methyl formate using $Ru_3(CO)_{12} + P(^cHx)_3$ as catalyst precursor at 180°C. Methyl formate is the source of CO, and H_2 is generated by the water gas shift reaction [66]. Aqueous methyl formate was used as a source of CO and H_2 *via* catalysis with $Ru_3(CO)_{12} + P(^cHx)_3$ in the hydroformylation of cycloalkenes and linear alkenes to alcohols. The hydroformylation reaction involves $[HRu_3(CO)_{11}]^-$ [67]. Hydroformylation of terminal and internal olefins using ruthenium melt catalyst in the presence of N- and P-containing ligands such as 2,2′-bipyridine, 2,2′-bipyrimidine, and 1,2-bis(diphenylphosphino)ethane gave 99% linear oxoalcohols and aldehydes [68]. See also [22,55].

2.2.5. Heterogeneous systems (supported complexes)

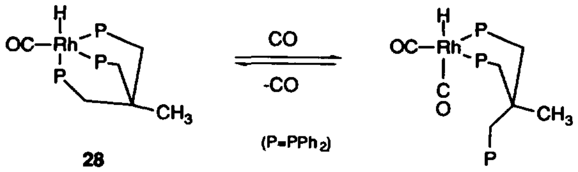
Several kind of polymer-supported transition metal complexes were examined in their hydroformylation catalytic performance for olefins including 1-hexene and diisobutene. Poly(N-vinylpyrrolidone) and maleic anhydride–styrene copolymer as supports and a Co–Rh bimetallic cluster catalyst showed the best activity and aldehyde selectivity [69]. Ethene hydroformylation over a Nafion-supported rhodium catalyst (prepared by ion exchange from $Rh(NO_3)_3$) has been studied under atmospheric pressure in the temperature range of 100–135°C. Hydrogenation to ethane was a significant side reaction [70]. Olefins were hydroformylated with the water-soluble $HRh(CO)[P(m\text{-}C_6H_4SO_3Na)_3]_3$ catalyst supported on a high surface area silica. It is proposed that the hydrophilic support holds the phosphine by hydrogen bonding of the hydrated sulfonate groups to the surface [71]. Hydroformylation of alkenes over heterogenized rhodium-phosphine-based catalysts was studied [72]. The hydroformylation of propene was studied at 90–120°C and 3–10 bar in the presence of silica-supported $HRh(CO)(PPh_3)_3$ as the catalyst, in an excess of liquid phosphine ($Me(CH_2)_nPPh_2$; $n = 3$, 7, 17; $(^cHx)_xPPh_{3-x}$; $x = 0$, 1, 2; allyl- and poly(butadienyl)diphenylphosphines) as solvent. The activity of the catalysts increases both with the mobility of the phosphine and with the lower electron density on the phosphorus [73]. Immobilized $HRh(CO)(P(m\text{-}C_6H_4SO_3Na)_3)_3$ on an anion exchange resin was used for the hydroformylation of higher olefins in anhydrous alcohol solvents. Activities and selectivities were similar to both supported aqueous-phase catalysts and to the neutral complex, $HRh(CO)(PPh_3)_3$ in nonaqueous solvents [74]. Bis(trisulfonated triphenylphosphine)platinum dichloride was supported on glass to yield an immobilized olefin hydroformylation catalyst. This catalyst combined with $SnCl_2$ afforded normal to branch ratios of up to 11.5 in hydroformylation of 1-hexene at 100°C and 70 bar [75]. Triruthenium ketenylidene cluster, $[PPN]_2[Ru_3(CO)_9(CCO)]$, deposited on MgO was found to show high activity and selectivity toward propanal in hydroformylation of ethene [76]. $RhCl_3 \cdot 3H_2O$ and $RhCl(CO)(PPh_3)_2$ were immobilized on a styrene–divinylbenzene copolymer containing $-CH_2-P(C_6H_4SO_3H)_2$ groups to give active hydroformylation catalysts in an aqueous phase for the propene hydroformylation at 100°C and 5–50 bar $CO + H_2$ pressure [77]. Improved methods for the preparation of rhodium-based supported aqueous phase hydroformylation catalysts were described [78]; using these catalysts the effect of temperature, pressure and water content in hydroformylation of linear, terminal and internal olefins was studied [79]. Polymer bonded $RhCl(CO)(PPh_3)_2$ was used to catalyze 1-hexene hydroformylation in liquid suspension phase and ethene hydroformylation in vapor phase. Control experiments showed the same activity of the immobilized catalyst and that of its homogeneous analog [80]. Rhodium clusters of the type $Rh_{55}L_{12}Cl_x$ ($L = P(^tBu)_3$, $x = 20$; $L = PPh_3$, $x = 6$) anchored on TiO_2 and Na–Y-zeolite were studied as hydroformylation catalysts for ethene and propene. No loss of activity even after 27 experiments was found if propene was hydroformylated in an aqueous medium [81].

2.3. Coordination chemistry related to hydroformylation

The kinetics of both the formation and the hydrogenolysis of $Me_3CCH_2CH_2C(=O)Rh(CO)_4$ have been studied during hydroformylation of $Me_3CCH{=}CH_2$ starting with $Rh_4(CO)_{12}$ as catalyst precursor at 4–20°C in n-hexane as solvent. The results support the classic mechanistic picture of the unmodified rhodium-catalyzed hydroformylation reaction [82]. The key intermediates in rhodium-catalyzed methanol carbonylation, $MeRh(CO)_2I_3^-$ and $MeC(=O)Rh(CO)I_3^-$ were detected using FTIR and FTNMR spectroscopy in neat MeI. From kinetic data in the range of 5–35°C $\Delta H^{\ddagger} = 63 \pm 2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -59 \pm 9$ J mol^{-1} K^{-1} were calculated for the crucial methyl migration step of the catalytic cycle [83].

Kinetics of the ring-opening carbonylation of ethyloxirane with $HCo(CO)_4$ was studied. The rate of CO uptake is first order with respect to $HCo(CO)_4$ and ethyloxirane, and independent of the concentration of $Co(CO)_4^-$ and CO. The reaction is faster with $DCo(CO)_4$. An ion pair formation and a rate-determining internal substitution followed by fast CO insertion was suggested as the mechanism [84]. The mechanism of H_2 activation in cobalt-catalyzed olefin hydroformylation was studied by high pressure IR spectroscopy using $HCo(CO)_4$ under 100 bar H_2 (or D_2) in the absence or presence of CO (0.65 bar and 2.3 bar) at 25°C. It was concluded that the activation of H_2 starts at a coordinative unsaturated acyl cobalt carbonyl yielding an aldehyde and a hydrido cobalt carbonyl species, probably $HCo(CO)_3$ [85].

Reversible arm-off dissociation of the tripodal $MeC(CH_2PPh_2)_3$ in **28** under $H_2/CO = 1/1$ at room temperature was established by high-pressure IR and ^{31}P NMR spectroscopy. It was suggested that the arm-off dissociation, depicted below, can rationalize the low n/i selectivities frequently observed in the catalytic hydroformylation of olefins using triphos-modified rhodium catalysts [86].

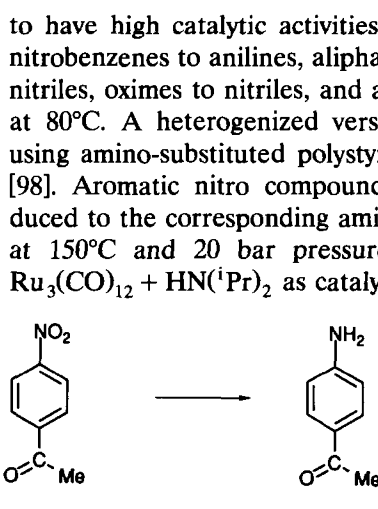


28

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

The kinetics of the water gas shift reaction catalyzed by rhodium(III) chloride in aqueous picoline were studied by using a continuous-flow stirred reactor [87]. The water gas shift reaction by $Ru_3(CO)_{12}$ + 2,2′-bipyridine catalyst on various inorganic supports was investigated in a flow reactor. The highest activity, 8170 mol H_2 mol^- $Ru_3(CO)_{12}$/24 h, was obtained using magnesium silicate carrier at 150°C [88]. The catalytic system $Ru_3(CO)_{12}$ + tricyclohexylphosphine was found to decarbonylate methyl formate into synthesis gas and, at the same time, catalyzed the water gas shift reaction [89]. Alkyl formates were rapidly decomposed to H_2, CO_2 and the corresponding alcohols using $Ru_3(CO)_{12}$ and KOAc as catalyst. Turnover rate as fast as 8446/h was observed for ethyl formate at 140°C [90]. The dehydroxylation of C_3–C_5 polyols and C_6 sugars with ruthenium iodocarbonyl catalyst in aqueous solution under 90 bar ($CO/H_2 = 2$) pressure at 200°C was studied. Glycerol gave n-propanol and its ethers with selectivities of up to 90%, and D-glucose afforded at 99% conversion 39.5% yield of γ-valerolactone [91]. An efficient water gas shift reaction was reported using dipyridyl iridium complexes as catalysts, visible light irradiation at room temperature, atmospheric pressure, and neutral pH [92]. Several transition metal catalysts were screened in order to obtain low-temperature sulfur-tolerant homogeneous catalysts for the water–gas shift reaction [93].

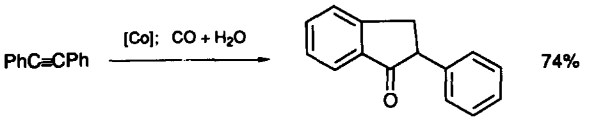
Selective catalytic reduction of aromatic nitro compounds to the corresponding amine using rhodium–phosphine and rhodium–amine complexes and the water–gas shift reaction at room temperature and atmospheric pressure of CO has been reported [94–96]. The highest turnover frequency (296 mol Rh^{-1} h^{-1}) was obtained in the reduction of *p*-nitroanisole using $Rh_6(CO)_{16}$ + 1,8-bis(dimethyl-amino)naphthalene + aqueous NaOH as the catalyst precursor in 2-methoxyethanol [95]. High catalytic activities for the selective reduction of aromatic nitro compounds to yield aromatic amines were found by using amine-added rhodium carbonyl complexes at room temperature and atmospheric pressure of carbon monoxide in 2-methoxyethanol or diglyme containing 5 equiv. NaOH and water. The highest activity was 1776 mol cat^{-1} h^{-1} in the case of the reduction of *p*-nitroanisole using $Rh_6(CO)_{16}$ + 1,8-bis(dimethylamino)naphthalene as catalyst [97]. A catalyst system of $Rh_6(CO)_{16}$ + N,N,N′,N′-tetramethyl-1,3-propanediamine was found to have high catalytic activities for the conversion of nitrobenzenes to anilines, aliphatic nitro compounds to nitriles, oximes to nitriles, and amine oxides to amines at 80°C. A heterogenized version of the catalyst by using amino-substituted polystyrenes was also studied [98]. Aromatic nitro compounds were selectively reduced to the corresponding amines with CO and H_2O at 150°C and 20 bar pressure in the presence of $Ru_3(CO)_{12} + HN(^iPr)_2$ as catalyst [99]. *E.g.*:



>99.9%

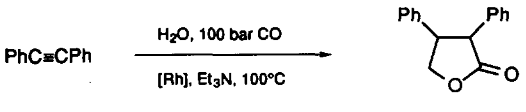
The influence of polar effects on the conversion and selectivity in the $Ru_3(CO)_{12}$-catalyzed reductive carbonylation of aromatic nitro derivatives to ureas and amines has been studied [100].

Selective synthesis of **29** from diphenylacetylene under water–gas shift conditions with a $Co_2(CO)_8 + PPh_3$ catalyst was achieved at 220°C and 100 bar CO pressure [101].



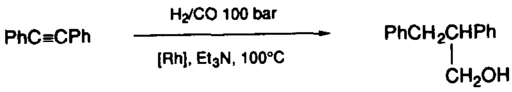
29

$Rh_4(CO)_{12}$-catalyzed carbonylation of internal acetylenes under water–gas shift reaction conditions gave selectively 3,4-disubstituted furan-2(5*H*)-ones. *E.g.*:



conv. 100%, selectivity 87%

Molecular hydrogen in place of water gave hydroxymethylated product [102]:



$$PhC{\equiv}CPh \xrightarrow[\text{[Rh], Et}_3\text{N, 100°C}]{H_2/CO \text{ 100 bar}} \underset{\displaystyle CH_2OH}{PhCH_2CHPh}$$

56% isolated yield

The role of alcohol in the catalytic reductive carbonylation of nitrobenzenes to carbamates in the presence of $Rh(CO)_4^-$ or $Ru_3(CO)_{12}$ was studied. The selectivity of N-phenylcarbamate in the reductive carbonylation of nitrobenzene at 27 bar CO and 140°C was much higher in t-butyl alcohol than in primary or secondary alcohol [103]. *E.g.*:

$$PhNO_2 + 3CO + t\text{-}BuOH \longrightarrow PhNHCOO\,t\text{-}Bu + 2CO_2$$

up to 97%

Mixtures of carbazole and *o*-aminodiphenyl were formed from *o*-nitrodiphenyl in acetonitrile at 200–220°C and 50 bar CO in the presence of $Ru_3(CO)_{12}$ as catalyst [104].

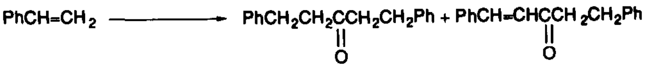
Rhodium carbonyl anions on aminated polystyrenes were tested as catalysts for water–gas shift reaction and for various deoxygenations. $Rh_6(CO)_{15}^{2-}$ and $Rh_6(CO)_{15}H^-$ on the polymer showed catalytic activities for reduction of nitrobenzene to aniline, aliphatic nitro compounds to nitriles, N-oxides to amines and hydroxyl-amines to amines under CO and H_2O at 40–80°C. $Rh_{14}(CO)_{25}^{4-}$ and $Rh_{14}(CO)_{25}H^{3-}$ on the polymer catalyzed the water–gas shift reaction at 100°C [105]. Rhodium carbonyl cluster anions in aminated polymers were examined as catalysts for the water–gas shift reaction and deoxygenation of various nitrogen–oxygen bonds. $Rh_{14}(CO)_{25}^{4-}$ and Rh_6 anion species were found to be active catalysts for the water–gas shift reaction and for the deoxygenation of N–O bonds (in aliphatic nitro compounds to nitriles, N-oxides to amines, and hydroxylamines to amines), respectively [106].

The water–gas shift reaction catalyzed by soluble organometallic complexes was studied in a continuous flow stirred reactor [107].

The reaction of methyl nitrite and CO gave ammonia in the presence of water vapor over $[RhCl_2(CO)_2]^-$ + C catalyst. The water–gas shift reaction is thought to be involved in the reduction [108].

1,2-Bis(phenyl)ethane derivatives were obtained from hydrobenzoin, 4,4′-dihydroxyhydrobenzoin and anisoin at 250 bar CO/H_2 at 180–200°C using cobalt acetate or cobalt carbonyl as the catalyst precursor [109].

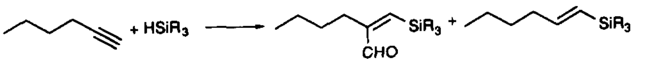
In the presence of $[(dppp)Pd(MeCN)_2][BF_4]$ as the catalyst (dppp = 1,3-bis(diphenylphosphino)propane), styrene in THF at 77°C and 160 bar $CO:H_2 = 1$ gave **30** and **31** (5:95 molar ratio) with a selectivity of ≈ 99% [110].



$$PhCH{=}CH_2 \longrightarrow PhCH_2CH_2\underset{\displaystyle \overset{\|}{O}}{C}CH_2CH_2Ph + PhCH{=}CH\underset{\displaystyle \overset{\|}{O}}{C}CH_2CH_2Ph$$

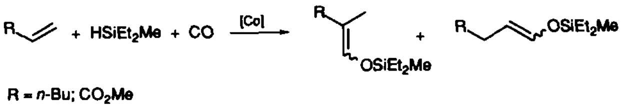
30 **31**

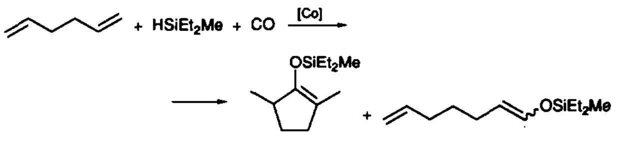
The $Co_2Rh_2(CO)_{12}$- and $Rh_4(CO)_{12}$-catalyzed silylformylation of 1-hexyne at 25°C in toluene under CO (1-10 bar) afforded **32** in good yields using alkyl- or alkylarylsilanes. In the case of R = OMe, **33** was obtained as the main product [111].



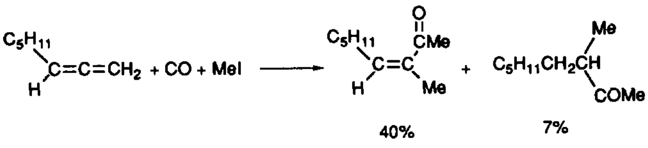
32 **33**

The effects of changes in reaction conditions (CO pressure, molar ratio of the reactants, and temperature) on the isomer composition of the $Co_2(CO)_8$-catalyzed reaction of 1-hexene, methyl acrylate, and 1,5-hexadiene with diethylmethylsilane and CO have been investigated [112]. The catalytic activity of various transition metal complexes was examined for the reaction of 1-hexene with $HSiEt_2Me$ and CO at 140°C. In addition to $Co_2(CO)_8$, $Co_2(CO)_8 + PPh_3$, $Co_2(CO)_8 + P(^nBu)_3$, $Ru_3(CO)_{12}$, $RhCl(PPh_3)_3$, and $RhCl(PPh_3)_3 + Et_3N$ precursors were found to give effective catalysts [112].



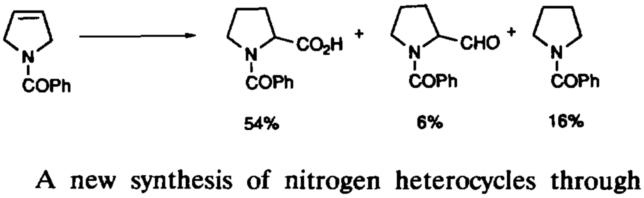


Allenes react with $Mn_2(CO)_{10}$, MeI and CO (1 bar) under mild phase transfer conditions to give (*Z*)-isomers of α,β-unsaturated carbonyls [113]. *E.g.*:

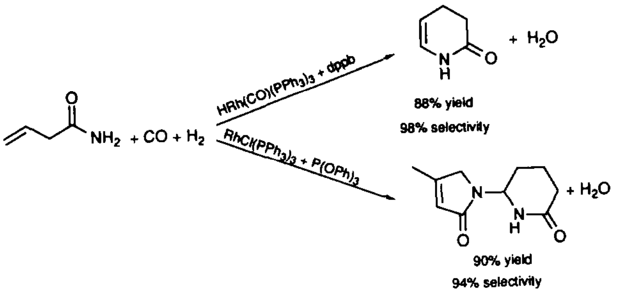


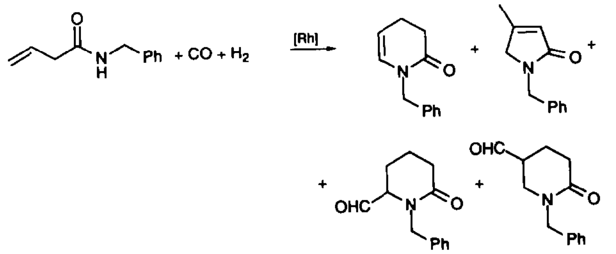
The reductive carbonylation of aryl- and alkyl-substituted alkenes at 100°C and 35 bar CO pressure in the presence of $NaBH_4$ and isopropanol and catalytic amount of $Rh(COD)(\eta^6\text{-}PhBPh_3)$ gave isomeric alcohols in up to 95% yield [114].

N-Acyl derivatives of proline and 2-piperidinecarboxylic acid were synthesized in moderate yield from N-acyl unsaturated cyclic amines by cobalt-catalyzed hydrocarboxylation in THF in the presence of water at 110°C and 120 bar $CO/H_2 = 1$ [115]. *E.g.*:

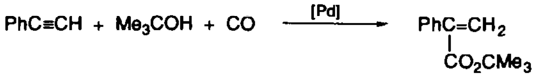


A new synthesis of nitrogen heterocycles through hydrocarbonylation of alkenamides catalyzed by Rh complexes such as $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, $HRh(CO)(PPh_3)_3$ and $Rh_4(CO)_{12}$ at 80–100°C and 80 bar $CO/H_2 = 1$ or 3 was reported [116]. *E.g.*:





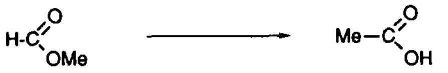
The hydroesterification of alkynes with carbon monoxide and alcohols using catalytic amounts of $Pd(dba)_2$ or $Pd(OAc)_2$ and 1,4-bis(diphenylphosphino)butane gave unsaturated esters at 150–190°C and 80 bar pressure in moderate yields [117]. *E.g.*:



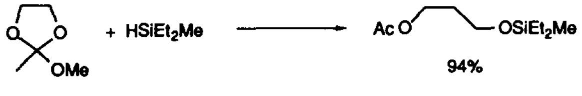
$$PhC{\equiv}CH + Me_3COH + CO \xrightarrow{[Pd]} PhC(=CH_2)CO_2CMe_3$$

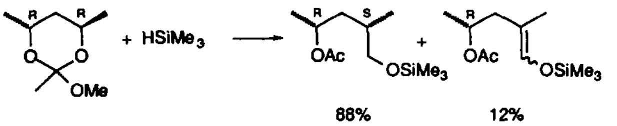
56%

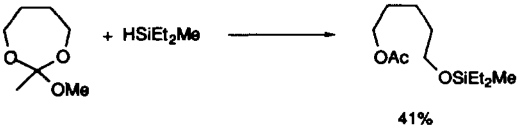
Methyl formate was selectively converted into acetic acid in quantitative yield in N-methylpyrrolidone between 160 and 180°C at > 100 bar CO pressure using $Co(OAc)_2 \cdot 4H_2O$ or $Co_2(CO)_8$ as catalyst precursor and alkali iodides as promoter [118].



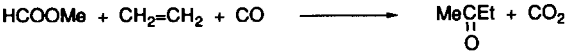
A new method for homologation of 1,2- 1,3-, and 1,4-diols *via* $Co_2(CO)_8$-catalyzed hydrosilylation under mild conditions (0–25°C, 1 bar CO, benzene or n-hexane solvent) was reported [119]. *E.g.*:







The reaction of methyl formate with a CO/C_2H_4 mixture (80 bar, 1/1) at 180°C in the presence of $RhCl_3 \cdot 3H_2O$ and LiI in N-methylpyrrolidone was found to give mainly methylethylketone and CO_2:



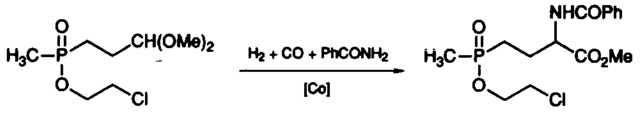
$$HCOOMe + CH_2{=}CH_2 + CO \longrightarrow Me\underset{O}{\overset{}{\underset{\|}{C}}}Et + CO_2$$

Propionaldehyde, methyl acetate, diethylketone, methyl propionate and methanol were side products in the reaction [120].

2.5. Hydroformylation-related reactions of CO

The $Co_2(CO)_8$-catalyzed aminocarbonylation of geminal dihaloalkanes at 100°C and 50 bar CO pressure to produce amides **34**, **35**, and **36** has been investigated. With $Ir_4(CO)_{12}$ and $Ru_3(CO)_{12}$ as the catalyst selective formation of $MeCH_2CONEt_2$ was obtained from $MeCHBr_2$ [121].

The $Co_2(CO)_8$-catalyzed amidocarbonylation of **8** at 120°C and 140 bar $CO/H_2 = 1$ in THF gave **37** in 85% yield [15].

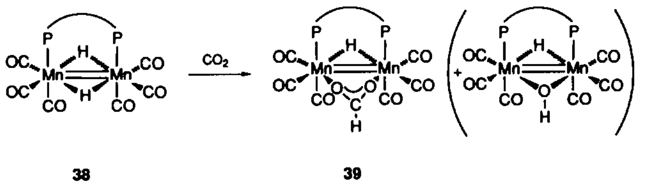


8 **37**

The cobalt-catalyzed amidocarbonylation of cyclopropanemethanol and α-methylcyclopropanemethanol gave N-acetyl-3-cyclopropylalanine and 2-acetamido-3-cyclopropylbutiric acid, respectively [122]. The amidocarbonylation of olefin and aldehyde substrates was applied to the synthesis of a variety of amidocarboxylic acids such as C_{14}–C_{16} N-acyl-α-amino acids, sarcosinates, and glutamic acid using cobalt, rhodium, or mixed-metal catalysts [123]. See also [102].

2.6. Reduction of CO_2

The coordinated CO_2 in $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}CO_2)$ was rapidly reduced to CO and H_2O at −78°C using excess $HCo(CO)_4$ or $H_2Fe(CO)_4$ as the reducing agent [124]. Carbon dioxide was reduced to methanol at an Everitt's soft-modified platinum electrode in the presence of cobalt(II)-2-nitroso-1-naphthol-4-sulfuric acid complex as the catalyst [125]. Carbon dioxide was reduced by **38** to a formate ligand in **39** at 50 bar pressure and room temperature [126].



38 **39**

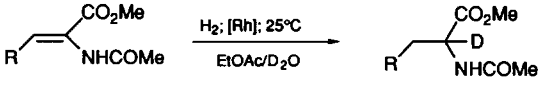
P-P = $Ph_2CH_2PPh_2$; $(EtO)_2POP(OEt)_2$

The catalytic reduction of carbon dioxide by H_2 in the presence of transition metal complexes was studied [127].

3. Hydrogenation and reduction

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

Hydrogenation of the methyl ester of α-acetamidocinnamic acid and α-acetamidoacrylic acid at 1–40 bar H_2 pressure at 25°C in an ethylacetate + deuterium oxide two-phase system, using an *in situ* catalyst prepared from $[Rh(COD)Cl]_2$ and various mono and disulfonated phosphines, has shown that only one deuterium atom is incorporated into the product **40** [128].

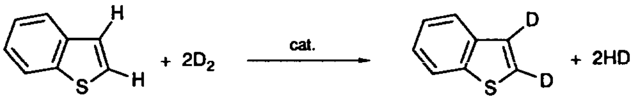


R = Ph, H

40

Hydrozirconation of (*E*)-3-methoxy-1-phenyl-1-propene and subsequent deuterolysis was found to give α- and ω-deuterated propylbenzenes after elimination of the ether function [129].

The H/D exchange in the reaction of EtOH and D_2 (1 bar) to give EtOD was catalyzed by $Ni(o\text{-}C_6H_4(OH)\text{-}CH{=}N\text{-}NHCSNH_2)_2Cl_2$ at 25°C [130]. The cationic complex $[(MeC_5H_4Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SH)]SO_3CF_3$ catalyzed the deuterium substitution of thiophene, methylthiophenes, and benzothiophene in CH_2Cl_2 solution at D_2 pressures of 3–4 bar and temperatures of 25–70°C [131]. *E.g.*:



>90%

Catalytic deuterium exchange between Ph_2SiH_2 and D_2 in the presence of $[(dippe)Rh]_2(\mu\text{-}H)_2$ (dippe = 1,2-bis(diisopropylphosphino ethane) was reported. $[(dippe)Rh]_2(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}HSiPh_2)$ and $[(dippe)Rh]_2(\mu\text{-}SiPh_2)_2$ were identified as the possible intermediates of the catalytic cycle. At 60°C and under dinitrogen $[(dippe)Rh]_2(\mu\text{-}H)_2$ catalyzes the dehydrogenative silicon–silicon coupling of Ph_2SiH_2 [132]:

$$2Ph_2SiH_2 \longrightarrow \underset{71\text{-}77\%}{Ph_2SiHSiHPh_2} + H_2$$

Catalytic H/D exchange between ROH and D_2 was studied in the presence of dihydrogen complexes of ruthenium and iridium. $[Ir(bq)(PPh_3)_3H(\eta^2\text{-}H_2)]SbF_6$ (bq = 7,8-benzoquinolinato) was found to be the most efficient catalyst [133].

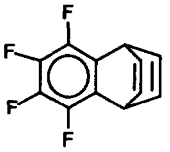
3.2. Hydrogenation of olefins

3.2.1. Fe, Ru, and Os catalysts

Olefins, diolefins and α,β-unsaturated ketones were hydrogenated at 60°C and 1 bar H_2 in ^{i}PrOH, toluene or 1,2-dichloroethane in the presence of catalytic amounts of $OsH_2Cl_2(P^iPr_3)_2$. The same complex in the presence of $NaBH_4$ also catalyzes the hydrogen transfer from ^{i}PrOH to benzylideneacetone resulting mainly in the saturated ketone [134].

The binuclear compounds $H(CO)(PPh_3)_2Ru(\mu$-bim)Ir(COD) (bim = 2,2′-biimidazolate) and $H(CO)(PPh_3)_2Ru(\mu$-pz$)_2$Ir(TFB) (pz = **41**, TFB = **42**) were found to be more active catalysts for the hydrogenation of cyclohexene at 60°C in toluene + ^{i}PrOH solution than the mononuclear parent compounds RuH(Hbim)(CO)$(PPh_3)_2$, Ir(Hbim)(COD), RuH(pz)(CO)(Hpz)$(PPh_3)_2$, and $[Ir(TFB)(Hpz)_2]BF_4$ [135].

41

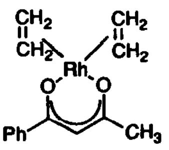


42

Poly(alkyl-substituted 1-pyrazolyl)boratoruthenium complexes were used to hydrogenate methyl acrylate and 3-phenylpropene at 50°C and 50 bar H_2 pressure [136]. See also [218].

3.2.2. Co, Rh, and Ir catalysts

Rhodium(I) complexes of β-diketonates have been found to be active catalysts for the hydrogenation of unhindered alkenes at 30°C and 1 bar H_2. Complex **43** effects the hydrogenation of 1-octene at a higher rate than that reported for the hydrogenation of the similar 1-hexene using $RhCl(PPh_3)_3$ [137].



43

Polystyrene-supported rhodium(I)-2,2′-bipyridine complex was found to be a good catalyst for hydrogenation of olefinic substrates, such as 1-hexene, cyclohexene, styrene, dimethyl fumarate *etc.*, at 35°C and 1 bar H_2 pressure [138]. The influence of concentrations on the rate of 1-octene hydrogenation in methanol solution using $Rh(PPh_3)_2(en)Cl$ (en = ethylenediamine) as catalyst precursor was studied [139]. Rhodium(I)-1,10-phenanthroline complex anchored to polystyrene was found to catalyze the hydrogenation of olefins (*e.g.*: 1-heptene, cyclohexene, styrene, diethyl fumarate) at 35°C and atmospheric pressure [140].

Cationic rhodium(I) complexes containing thiophosphine ligands were checked as hydrogenation catalysts of 1-hexene to hexane at 1 bar H_2 pressure and 25°C, and of ketones to the corresponding alcohols in boiling isopropanol [141]. A comparison of $[Rh(COD)\{HC(PPh_2)_3\}]BF_4$ and $[Rh(COD)\{HC(PPh_2)_3\}Au(PPh_3)](BF_4)_2$ as catalyst precursors in 1-hexene hydrogenation at 25°C and 1 bar H_2 pressure has shown that the heterobinuclear system exhibits a longer induction period and a longer lifetime than the mononuclear one [142]. The complex $[(NBD)Rh(\text{n-phophos})_2]^{3+}$ (n-phophos = $[Ph_2P(CH_2)_nPMe_3]^+$; $n = 2$, 3, 6, 10) were found to be active olefin hydrogenation catalysts at 25°C in aqueous and aqueous-organic biphasic systems for maleic acid and 1-hexene, respectively [143].

Rhodium complexes with 2-(3-triethoxysilylpropyl)-aminocarbonylpyrrolidine, anchored on silica and modified Y-zeolite were found as efficient catalysts for hydrogenation of olefins at 50°C or 100°C and 6 bar H_2 pressure [144].

The rhodium(II) complex $[(^cHx)_3P]_2RhHCl_2$ was found to be an effective catalyst precursor for the hydrogenation of the double bond of α,β-unsaturated aldehydes and ketones under mild conditions in a biphasic system [145].

The kinetics of hydrogenation of fumaric acid, maleic acid, and crotonic acid in aqueous and aqueous-organic biphase systems using *in situ* prepared rhodium complex of sulfonated triphenylphosphine as the catalyst were studied [146].

Polystyrene-supported Rh^I bidentate ligand complexes (ligand = anthranilic acid, 2,2′-bipyridine or 1,10-phenanthroline) were used to catalyze the hydrogenation of terminal, cyclic and internal monoolefins, and dienes like ethyl sorbate [147].

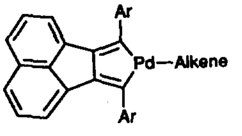
The unstable complexes $RhH_2(SR)(PPh_3)_3$ (R = ^{i}Pr, n-dodecyl, and C_6F_5) formed by the reaction of RSH with $Rh(PPh_3)_4$ were found to catalyze the homogeneous hydrogenation of cyclohexene at ambient temperature and pressure [148].

Hydrogenation of acrylic acids catalyzed by complexes of rhodium(I) containing mixed anhydrides of acrylic and diphenylphosphinous acids was studied [149]. See also [128,221,225].

3.2.3. Ni, Pd, and Pt catalysts

Palladium chloride anchored to a styrene-divinylbenzene copolymer matrix containing 8-aminoquinoline groups and reduced with different reducing agents was used as a catalyst for the hydrogenation of 1-hexene and cyclododecatriene. Factors affecting the loss of Pd from the catalyst were studied [150].

Zerovalent palladium complexes **44** were found to catalyze the homogeneous hydrogenation of the carbon–carbon double bond in α,β-unsaturated carbonyl compounds at 20°C and 1–1.5 bar H_2 pressure in THF solution [151].



Ar = Ph, p-MeC_6H_4, p-$MeOC_6H_4$

Alkene = dimethyl fumarate, fumaronitrile, maleic anhydride

44

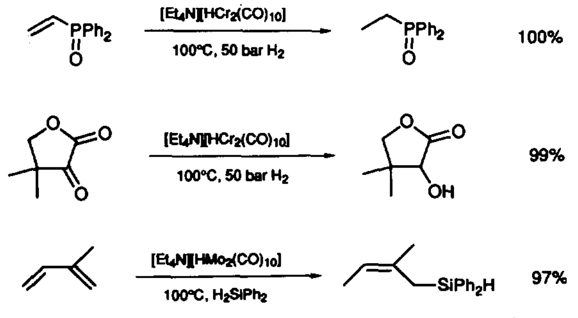
Hydrogenation of nitrile rubber using a 6-membered cyclopalladate complex of 2-benzoylpyridine as the catalyst was investigated. Hydrogenation occurred at the double bonds and there was no reaction of the nitrile groups [152].

1-Hexyne was used as a promoter for a $PdCl_2 + C_8H_{17}NH_2 + Et_3Al$ catalyst system in the hydrogenation of olefins [153]. See also [55].

3.2.4. Other metals as catalysts

The hydrogenation of naphthalene to tetralin was catalyzed by $(OAr)_2Ta(H)_3(PMe_2Ph)_2$ (OAr = 2,6-dicyclohexylphenoxide) in cyclohexane at 90°C and 80 bar H_2 pressure [154].

Anionic μ-hydride complexes $[HM_2(CO)_{10}]^-$ (M = Cr, Mo, W) have been found to catalyze the hydrogenation of conjugated olefins, aldehydes, ketoesters, and alkynes, and the hydrosilylation of aldehydes and conjugated olefins with high regio- and stereoselectivity [155]. *E.g.*:



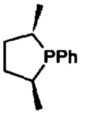
The hydrogenation of 1-decene using Cp_2ZrCl_2 + EtMgBr catalyst system gave near quantitative yields of decane at 50°C and 1 bar H_2 [156]. Catalytic reductions of α,β-unsaturated ketones using soluble copper(I) hydride complexes were studied [157]. Cyclohexene and benzene was hydrogenated to cyclohexane at 230°C and 100 bar H_2 using $Re_2(CO)_{10}$ as the catalyst precursor. In each case $Re_2(CO)_{10}$ was transformed into a new Re carbonyl compound, but this compound was different for the cyclohexene and benzene reaction [158]. Catalytic hydrogenation of 1-hexene in the presence of $[\{(CH_2)_3Cp_2\}LnH(THF)]_2$ (Ln = Y, Dy, Er, Lu) was reported [159].

3.3. Asymmetric hydrogenation of prochiral compounds

3.3.1. Asymmetric hydrogenation of olefins

Rhodium complexes with new chiral phospholane ligands, such as **45**, **46**, and **47**, were prepared and shown to act as efficient catalyst precursors for the enantioselective hydrogenation of various unsaturated substrates. The best results in hydrogenation of methyl acetamidocinnamate and dimethyl itaconate were obtained by using the ligand **47** at 20–25°C and 2 bar H_2 in 0.25–0.35 M methanol solutions of substrate with 0.1 mol% catalyst $[(COD)Rh(ligand)_2]^+SbF_6^-$, leading to 89% (*S*) and 94% (*S*) ee, respectively. Relatively low enantioselectivities were obtained in hydrogenation of acetophenone and methyl-3-oxobutyrate (6–27% ee) [160].

Asymmetric hydrogenation using a resolved chiral scandium hydride complex was studied [161].



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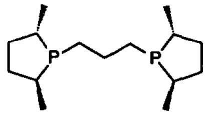

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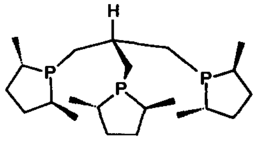
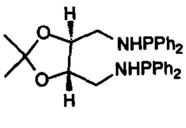


47

Derivatives of α-acetamidoacrylic acid were hydrogenated with $[Rh(L)(COD)]ClO_4$ (L = **48**) as the catalyst. Optical yields between 10–26% were achieved [162]. The DIOP-analog chiral diphosphine **49** was prepared and successfully used as ligand in the asymmetric hydrogenation of itaconic acid derivatives with Rh^I complexes as catalysts [163].



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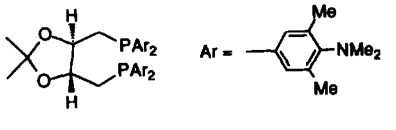
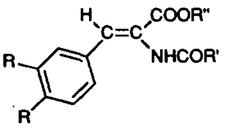


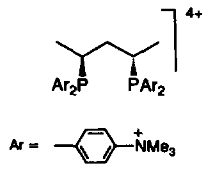
49

The dehydroamino acids **50** were hydrogenated using rhodium complexes of the chiral cationic phosphine **51**. The catalytic reactions were done either in a two-phase system with the catalyst in the aqueous phase or as a slurry in water. A necessary conditions in the latter case is theat the substrate has some water solubility. Enantioselectivities were as high as 95% [164].



R = H, MeO; R' = Me, Ph; R" = H, Me

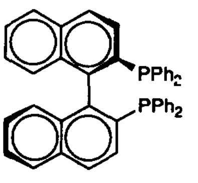
50



51

Asymmetric hydrogenation of (*Z*)-3,4-$(MeO)_2C_6H_3CH{=}C(NHCOR)COOR'$ (R = Me, Ph; R′ = Me, H) with the catalyst system composed of $[Rh(NBD)_2]PF_6$ and (*R*)-PROPHOS or (*R*)-BINAP gave the corresponding (*S*) saturated product [165].

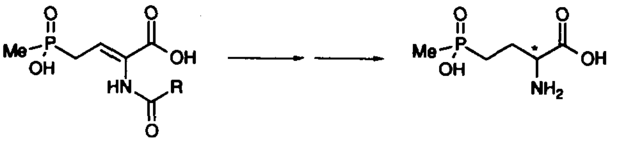
The rate law for the catalytic asymmetric hydrogenation of α,β-unsaturated carboxylic acids (such as methacrylic acid, tiglic acid, and 2-(6-methoxy-2-naphthyl)-acrylic acid) in methanol was found to be: rate = $k_{obs}[Ru^{II}(BINAP)(OAc)_2][substrate][H_2]/[substrate]_0$ (BINAP = **52**). Based on this rate law and on the results of labeling studies, it was concluded that the turnover-limiting step of the reaction is the heterolytic splitting of H_2 by a substrate-containing Ru-complex to form a metal hydride [166].



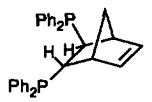
(*R*)-(+)-BINAP

52

The catalytic enantioselective synthesis of L-**54** and D-**54** by asymmetric hydrogenation of the precursor **53** was studied. Highest enrichment of L-**54** (90.8% ee) and D-**54** (91% ee) was achieved with *in situ* (*R*,*R*)-NORPHOS-chloro-norbornadiene-rhodium dimer catalyst and (*S*,*S*)-CHIRAPHOS-derived catalyst, respectively, at 25–50°C and 2.5–3.0 bar H_2 pressure in methanol {(*R*,*R*)-NORPHOS **55**; (*S*,*S*)-CHIRAPHOS **56**} [167].

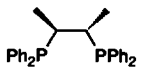


53 **54**



(*R*,*R*)-NORPHOS

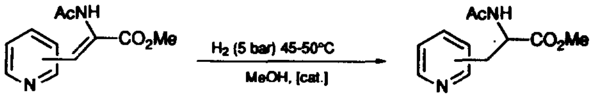
55



(*S*,*S*)-CHIRAPHOS

56

The D and L isomers of 3- and 4-pyridylalanine were prepared in 60–91% yield and 86–99% ee by asymmetric catalytic hydrogenation of the corresponding prochiral enamides **57** using (*S*,*S*)- or (*R*,*R*)-$[Rh(DIPAMP)(COD)]^+[BF4]^-$ as a catalyst (DIPAMP = **58**) [168].



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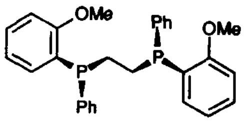
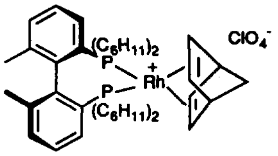


58

Up to 65% enantioselectivity was observed in the highly diastereoselective catalytic hydrogenation of racemic mixtures of α-pinene and of camphene using chiral ruthenium clusters such as $HRu_3(CO)_9(\mu_3,\eta^2\text{-}NEtCOOR)$ or $Ru_2(CO)_4(N_2,\eta^2\text{-}OOCR)_2(diphos)$ as the catalyst at 50 bar H_2 pressure [169].

$[Rh(C_5R_4R^*)Cl_2]_2$ (R = H, R* = neomenthyl; R = Me, R* = menthyl) were tested as hydrogenation catalysts in the presence of Et_3N. In the case of prochiral olefins only low optical induction was achieved [170]. The dinuclear rhodium complex (+)-*cis*-$[(^tBu_3As)(CO)Rh]_2(\mu\text{-}Cl)(\mu\text{-}SR)$ (R = 5β-methyl-2α-(1-methylethyl)cyclohexyl) was found to be a highly active hydrogenation catalyst for unhindered alkenes. In the case of N-acetamidocinnamate a good yield but low ee was obtained [171]. Chiral cationic and neutral Rh complexes **59** and **60** were found to be highly active and excellent catalysts for enantioselective hydrogenation of prochiral olefins and a ketone under mild reaction conditions. Thus the hydrogenation of (*Z*)-α-(benzamido)cinnamate in toluene at 25°C and 1 bar H_2 in the presence of **59** afforded (*S*)-$PhCH_2CH(COOEt)$-NHCOPh in > 99% ee. From itaconic acid under the same conditions, but using **60** as catalyst (*R*)-(+)-methylsuccinic acid was formed in 96% optical yield. The neutral Rh complex **60** converted N-benzylphenylglyoxylamide into the corresponding (*S*)-N-benzylmandelamide in quantitative yield with 89% optical purity [172].



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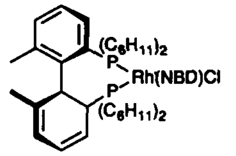
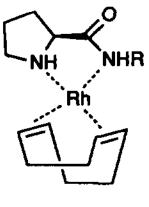


60

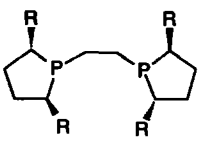
A comparison of the enantioselectivities in catalytic hydrogenation of N-acyldehydrophenylalanine derivatives at 65°C and 5 bar H_2 pressure, using **61** or its silica supported or zeolite supported variation as the catalyst, have shown that the zeolite-anchored one is superior leading to > 95% ee of N-acylphenylalanine derivatives [173].

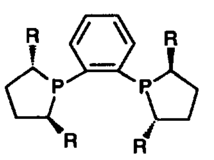


R = CMe$_3$, (CH$_2$)$_3$Si-{Sup}

61

Highly enantioselective (up to 99% ee) hydrogenations of acetamidoacrylates and enol acetates were reported using $[(COD)Rh(P_2)]^+OTf^-$ (P_2 = **62** or **63**) as catalyst precursor at 20–25°C and 2 bar H_2 [174].



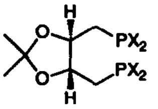


R = Me, Et, *i*-Pr

Heterogenized cationic rhodium(I) chelates of phenyl 4,6-*O*-(*R*)-benzylidene-2,3-bis(*O*-diphenylphosphino)-*β*-D-glucopyranoside on silica showed enhanced enantioselectivity in the hydrogenation of N-acetylamino-acrylic acid esters of up to 95% ee [175].

The results of the homogeneous asymmetric hydrogenation of several dehydroamino acids by rhodium-diene complexes of the chiral ligands **64**, **65**, **66** and their quaternized analogs were reported [176].

X = p-$C_6H_4NMe_2$; $[p\text{-}C_6H_4NMe_3]^+BF_4^-$; $[p\text{-}C_6H_4NHMe_2]^+BF_4^-$



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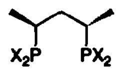

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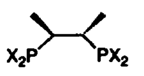
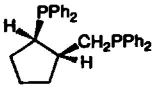


66

A rhodium complex with a new bisphosphine ligand **67** was found to be one of the most efficient catalysts for asymmetric hydrogenation of amino acid precursors such as (*Z*)-2-acetamidocinnamic acid [177]. The catalytic asymmetric hydrogenation of *α*-acetamidocinnamic acids in the presence of a Rh complex catalyst using Deguphos® (**68**) as chiral ligand was discussed. Advantages of the method were outlined [178].



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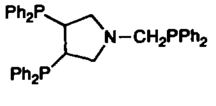
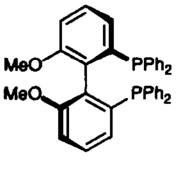


68

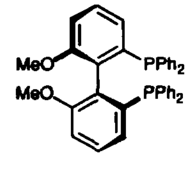
New chiral ruthenium-complexes containing DIOP, CHIRAPHOS, NORPHOS, and BINAP ligands were found to be effective for the asymmetric hydrogenation of unsaturated carboxylic acids to give the corresponding saturated derivatives with 90% ee [179].

Chiral (*S,S*)-(EBTHI)ZrMe$_2$ (EBTHI = ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl)) in combination with $[PhMe_2NH][Co(C_2B_9H_{11})_2]$ was found to be an effective asymmetric hydrogenation catalyst for 2-phenyl-1-butene to (*S*)-(+)-2-phenylbutane (91% yield, 23% ee) at room temperature under 100 bar H_2 [180].

The synthesis of (*R*)-**69** and (*S*)-**69** was described. These ligands were reported to lead to asymmetric inductions of 97–98% ee in ruthenium(II)-catalyzed enantioselective hydrogenations of allylic alcohols and of one *β*-keto ester [181].

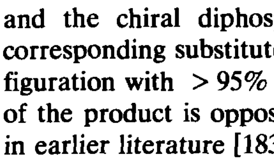


(*R*)-**69**



(*S*)-**69**

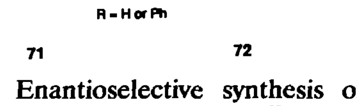
The ruthenium(II) complexes of (*R*)-**70** were found to be excellent catalysts in asymmetric hydrogenations of methyl 3-oxobutanoate and tiglic acid affording (*R*)-methyl 3-hydroxybutanoate (95–99% ee) and (*R*)-2-methylbutyric acid (86–91% ee), respectively [182].



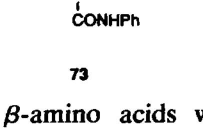
Ar = Ph or 4-MeOC$_6$H$_4$

70

Asymmetric hydrogenation of itaconic acids **71** in MeOH/C$_6$H$_6$ at 20°C and 1 bar H$_2$ in the presence of a neutral Rh complex prepared from $[Rh(COD)Cl]_2$ and the chiral diphosphine ligand **73** afforded the corresponding substituted succinic acids **72** of (*S*)-configuration with > 95% ee. The absolute configuration of the product is opposite to the one stated by others in earlier literature [183].

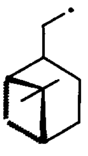


71 **72**



73

Enantioselective synthesis of *β*-amino acids was achieved by BINAP-Ru^{II} catalyzed hydrogenation of *β*-substituted (*E*)-*β*-(acylamino)acrylic acids. BINAP-Rh^I complexes afforded only moderate stereoselectivity with the opposite sense of enantioselection [184]. The enantioselective hydrogenation of methyl *α*-acetamidocinnamate in the presence of $[(^tBu)_3P(CO)Rh]_2(\mu\text{-}Cl)(\mu\text{-}SR^*)$ (R^* = **74** or **75**) attached to divinylbenzene-crosslinked polystyrene resins as the catalyst was studied. Optically active N-acetylphenylalanine methyl ester, up to 50% ee, was obtained [185].



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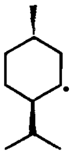
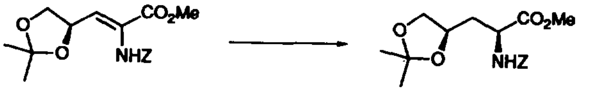


75

Complexes generated *in situ* from rhodium(I) dicarbonyl acetylacetonate and diphosphine were found to catalyze the hydrogenation of α,β-unsaturated aldehydes and ketones into the corresponding saturated carbonyl compounds. Using (−)-DIOP, geranial was hydrogenated into (+)-citronellal (62% ee) and neral into (−)-citonellal (55% ee) [186].

High diastereoselectivity (> 99.5%) was observed in the hydrogenation of **76** and **77** at room temperature and 3 bar H_2 in the presence of (*R,R*)-$[Rh(1,5\text{-}COD)(DIPAMP)]^+BF_4^-$ as the catalyst [187].



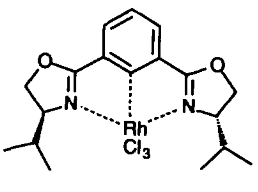
76

Z = $PhCH_2OC(=O)$; Boc = $Me_3COC(=O)$

77

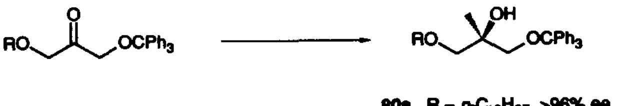
3.3.2. Asymmetric hydrogenation of ketones

Extremely high enantioselectivities (up to 99% ee) in the reduction of aromatic and aliphatic ketones with diphenylsilane using **78** and $AgBF_4$ as the catalyst precursor have been reported [188].



78

In the presence of BINAP-Ru-catalyst, **80** was prepared by asymmetric hydrogenation of the corresponding ketone **79** at 25°C and 100 bar H_2 pressure [189].



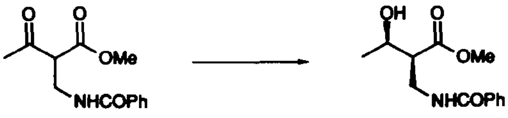
79

80a R = $n\text{-}C_{18}H_{37}$ >96% ee
80a R = CH_2Ph 87-88% ee

Highly enantioselective reduction of β-keto esters to the corresponding alcohol was achieved by using the BINAP-Ru-catalyst at 3 bar H_2 pressure and 80°C [190]. *E.g.*:

96% yield, 98% ee

Detailed description of convenient preparations of the BINAP-Ru^{II}-catalyst and its application in the highly enantioselective hydrogenation of methyl 3-oxobutanoate at 100 bar and 25°C and at 4 bar and 100°C was disclosed [191]. Highly diastereoselective hydrogenation of **81** was accomplished at 50–60°C and 50 bar H_2 pressure by using [RuI{(*R*)-BINAP}(*p*-cymene)]I and corresponding complexes of derivatives of BINAP as catalyst, giving **82** in up to 98% diastereomeric excess and 99% ee [192].



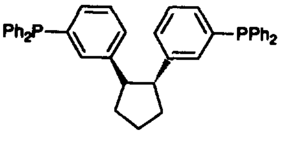
81 **82**

Asymmetric hydrogenation of **83** at 100 bar H_2 and 50°C using $Ru_2Cl_4((S)\text{-}BINAP)_2(NEt_3)$ as the catalyst gave predominantly **84** [193].

83 **84**

Asymmetric hydrogenation of α-keto esters and α-keto amides in the presence of alkylaminophosphinephosphinite rhodium complexes as catalysts was studied. Under ambient conditions and at a substrate/catalyst ratio of 10,000 up to 90% ee was achieved [194].

The chiral bisphosphines **85** and **86** were prepared in optically pure forms based on asymmetric hydrogenation of 4,5-diaryl-2-oxocyclopentanecarboxylates catalyzed by the (*S*)-BINAP-Ru^{II}-complex **87** [195].



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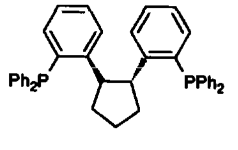

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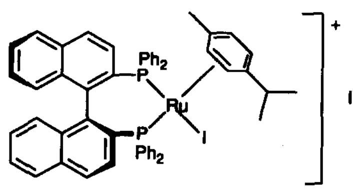
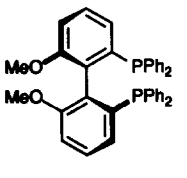


The high efficacy of preformed and *in situ* generated Ru^{II} complexes with atropisomeric diphosphine **88**, **89**, **90**, and **91** as precatalyst was demonstrated in asymmetric hydrogenations of allylic alcohols, enamides, and a β-keto ester. Quantitative chemical yields and 95–99% optical yields were reported [196].



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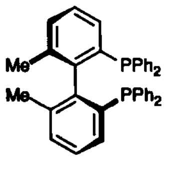

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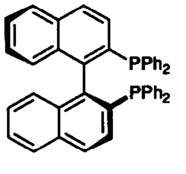

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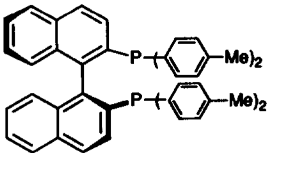
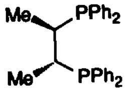


91

Racemic 2-acylamino-3-oxobutyrates were hydrogenated stereoselectively *via* dynamic kinetic resolution with various chiral rhodium and ruthenium catalysts to give *syn* optically active alcohols. The best results were obtained using ruthenium complexes of (*S*)-BINAP (**90**) and (*R*,*R*)-CHIRAPHOS (**92**) as catalysts [197].



92

See also [172,181,182].

3.3.3. *Asymmetric hydrogenation of imines*

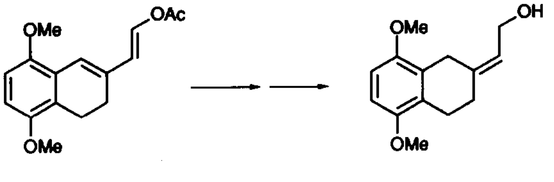
The imines ArC(Me)=NCH$_2$Ph (Ar = Ph, 2-MeO-C_6H_4, 3-MeO-C_6H_4, 4-MeO-C_6H_4) were hydrogenated to the corresponding amines with enantioselectivities up to 96% at 20°C and 70 bar H_2 using rhodium complexes associated with sulfonated bdpp (bdpp = (−)-(2*S*,4*S*)-2,4-bis(diphenylphosphino) pentane) [198].

Catalytic asymmetric hydrogenation of imines using an *in situ* Rh^I catalyst formed from $[Rh(NBD)Cl]_2$ and cycphos (1,2-bis(diphenylphosphino)-1-cyclohexyl-ethane) was studied in 1:1 benzene/methanol under 70–100 bar H_2 from −25 to +25°C. A maximum of 91% ee was obtained for 4-MeOC$_6$H$_4$C(Me)=NCH$_2$Ph in the presence of iodide cocatalyst at −25°C [199].

3.4. *Hydrogenation of dienes and alkynes*

A $(Na^+)_4(FePc^{4-})$/NaY electron donor-acceptor (EDA) complex was prepared from NaY zeolite-encapsulated Fe phthalocyanine (FePc) by reaction with Na-naphthalide. The encapsulated EDA complex gave a higher *trans*/*cis* ratio of 2-butene in hydrogenation of butadiene than the same complex on the external surface of NaY [200]. A catalyst prepared from $(\pi\text{-}C_3H_5PdCl)_2$ and octylamine was found to be an active and selective catalyst for the hydrogenation of alkynes and conjugated dienes to monoolefins. Activities exceeding 30,000 mols of substrate per mol Pd were obtained at room temperature and atmospheric pressure [201]. The hydrogenation activity of palladium ferrocenyl amine sulfide complexes at room temperature and 5 bar H_2 pressure has been probed with dienes and styrene derivatives [202].

Hydrogenation of **93** in the presence of naphthalene-Cr(CO)$_3$ complex as the catalyst afforded **94** after deacetylation [203].



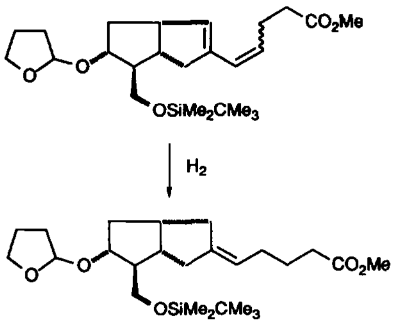
93 **94**

The *fac*-Cr(CO)$_3$(η^4-NBD) species was invoked as an intermediate in the formation of nortricyclene, the major product of the photocatalytic hydrogenation of NBD [204]. The known photocatalytic hydrogenation of norbornadiene (NBD) in the presence of $Cr(CO)_6$ or Cr(CO)$_4$(η^4-NBD) leading to norbornene and nortricyclene was performed in the dark at 20°C by substituting the catalyst precursor by *mer*-Cr(CO)$_3$(η^4-NBD)(η^2-ethene). From the observed pressure dependence and labelling experiments it was concluded that the catalytically active complex is **95** and **96** for norbornene and nortricyclene formation, respectively [205].

95

96

Tricarbonylchromium(0) encapsulated in NaX zeolite was found to be an extremely active catalyst in butadiene hydrogenation at room temperature, whereas $Cr(CO)_4$ + NaX showed only photoassisted hydrogenation activity during UV irradiation [206]. The methyl benzoate-Cr(CO)$_3$ complex was used to catalyze the 1,4-hydrogenation of **97** to afford **98** [207].

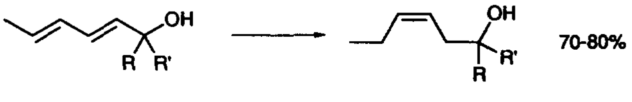


97

98

Homogeneous catalytic hydrogenation and hydrosilylation of diene polymers by transition metal catalysts were studied [208]. The catalytic activity of phosphorus-bridged iron and ruthenium clusters in the homogeneous hydrogenation of diphenylacetylene was studied. Considerable activity was found in the case of $Ru_4(CO)_{13}(\mu_3\text{-PPh})$, but the outcome depends markedly on the reaction time and temperature [209].

Selective hydrogenation of **99** in hexane with $Cr(CO)_6$ as the catalyst gave **100** in good yield [210].



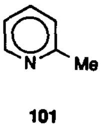
99 **100**

(R = H, R' = H, Me, CH_2CHMe_2; R = Me, R' = Me, Et, Ph)

3.5. Hydrogenation of arenes and heterocyclic compounds

Several complexes of group VIII metals have been tested as catalysts for the hydrogenation of benzene and its derivatives as well as for hydrogenation of coal in acidic medium. The system $[RhCl_2(2\text{-methylallyl})]_x$ + $P(2\text{-pyridyl})_3$ was found to be the most active for the hydrogenation of benzene [211].

The regioselective hydrogenation of mono- and polynuclear heterocyclic compounds **101-107**, as coal model compounds, was studied in CH_2Cl_2 at 40°C and 30 bar H_2 (or D_2) with $Cph(MeCN)_3^{2+}$ as the catalyst precursor. The order of relative rates was found to be **105** ⋙ **106** > **102** > **104** > **103** > **107** ≫ **101** [212].



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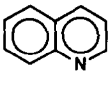

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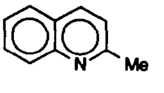

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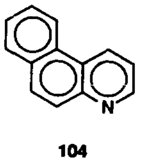

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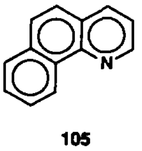

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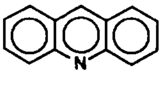

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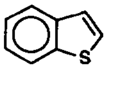


107

The catalytically inactive cobalt hydride, $[(dippp)Co]_2(H)(\mu\text{-}H)_3$, formed upon hydrogenation of aromatic substrates using the cobalt catalyst precursor $(\eta^2\text{-}C_3H_5)Co(dippp)$ has been characterized [213]. (dippp $= {}^iPr_2P(CH_2)_3P^iPr_2$).

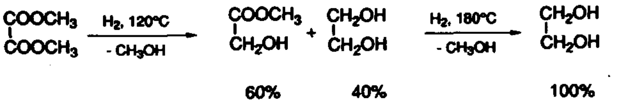
The platinum complex $PtCl_2(CH_3CN)_2$ dissolved in $BF_3 \cdot H_2O$ and supported on kieselgel catalyzes the hydrogenation of benzene, toluene, *o*-xylene, and naphthalene at 25°C and 28 bar H_2 pressure [214].

The cationic ruthenium arene complex $[RuH(PPh_3)_2(\eta^6\text{-9,10-dimethylanthracene})]^+$ was found to catalyze the hydrogenation of 9,10-dimethylanthracene. The rate law for the first step, the hydrogenation to 1,2-dihydro-9,10-dimethylanthracene was determined [215]. See also [158].

3.6. Hydrogenation of carbonyl compounds

The cationic ruthenium hydride complexes $[HRu(PR_3)_3]^+(OTs)^-$ and $[H(H_2)Ru(PR_3)_3]^+(PF_6)^-$ exhibit high catalytic activities for the hydrogenation of acetophenone [216].

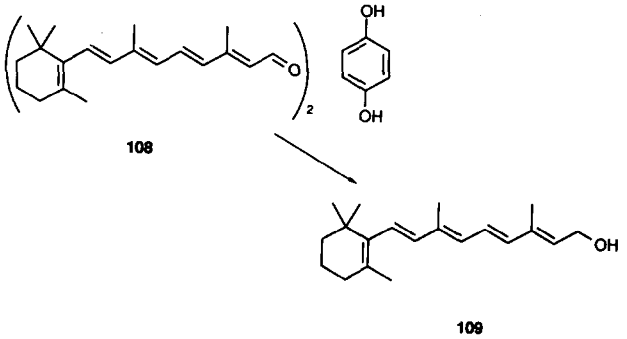
Dimethyl oxalate was selectively hydrogenated at 200 bar pressure to ethylene glycol in to steps in the presence of $Ru_2(CO)_4(CH_3COO)_2(P^iPr_3)_2$ [217].



$$\begin{matrix}COOCH_3\\ |\\ COOCH_3\end{matrix} \xrightarrow[-CH_3OH]{H_2,\ 120°C} \underset{60\%}{\begin{matrix}COOCH_3\\ |\\ CH_2OH\end{matrix}} + \underset{40\%}{\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix}} \xrightarrow[-CH_3OH]{H_2,\ 180°C} \underset{100\%}{\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix}}$$

$Ru_3(CO)_{12}$-phosphine (or phosphite) were found to be effective catalytic systems for the selective hydrogenation of α,β-unsaturated aldehydes at 110°C and 30 bar H_2 pressure. Selectivity varies with the $P/Ru_3(CO)_{12}$ ratio. With a low ratio the carbon–carbon double bonds are preferentially reduced. High ratios lead to the selective hydrogenation of the carbonyl groups [218].

The regioselective and stereospecific hydrogenation of the hydroquinone all-*trans*-retinal complex **108** to all-*trans*-retinol **109** has been achieved using $H_2Ru(PPh_3)_4$ as the catalyst [219].

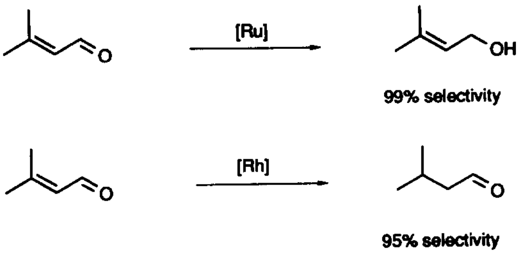


108

109

Ruthenium and osmium arsine complexes were found to catalyze the hydrogenation of propionaldehyde to propanol at 130°C and 30 bar H_2 pressure [220].

Selective hydrogenation of α,β-unsaturated aldehydes catalyzed either by ruthenium or rhodium sulfonated phosphine complexes under biphasic conditions was reported. 3-Methyl-butenal was reduced either into 3-methyl-2-butenol with the Ru + TPPTS system or into 3-methyl-butanal with Rh + TPPTS (TPPTS = tris(*m*-sulfophenyl)phosphine trisodium salt) [221].

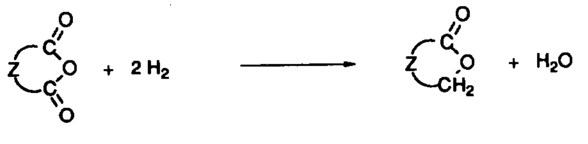


Hydrogenation of benzylideneacetone catalyzed by iridium complexes formed *in situ* from [Ir(COD)(OMe)]$_2$ and P(*o*-$C_6H_4NH_2$)Ph_2 or P(*o*-$C_6H_4NMe_2$)Ph_2 was investigated. Selective carbonyl-hydrogenation was achieved using the former ligand in a 5/1 = P/Ir ratio at 20 bar H_2 and 100°C [222].

The catalytic activity of $OsHCl(CO)(AsPh_3)_3$, $OsHCl(CO)(AsPh_3)(Ph_2P\text{-}CH_2CH_2AsPh_2)$ or $OsCl(CO)(OAc)(AsPh_3)_2$ in the hydrogenation of propanal to give n-propanol was reported [223].

The cationic iridium(I) complex $[Ir(COD)(PPh_3)(PhCN)]ClO_4$ was found to catalyze the hydrogenation of α,β-unsaturated aldehydes, PhCH=CRCHO (R = H, Me or Cl) to give $PhCH{=}CRCH_2OH$, $PhCH_2CHRCHO$ and $PhCH_2CHRCH_2OH$ at 50°C and 6 bar H_2 [225].

Cationic ruthenium complexes, prepared *in situ* from $Ru(acac)_3$ and phosphines, showed high activity and selectivity in hydrogenation reaction of carboxylic anhydrides at 200°C and 30 bar H_2 pressure in the presence of a strong acid such as *p*-toluenesulfonic acid [226].



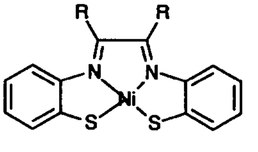
(Z = 2 CH_3, -$(CH_2)_2$-, -C_6H_4-)

Polysiloxane-supported ruthenium complexes were found to be active in hydrogenation of crotonaldehyde to crotyl alcohol at 120°C and 50 bar H_2 [227]. See also [141,155].

3.7. Hydrogenation of nitro compounds

A cyanoethyl cellulose-supported $PdCl_2$ catalyst for hydrogenation of nitrobenzene to aniline was prepared and characterized. The catalyst showed great activity and stability and could be reused many times. Aliphatic nitro compounds had very slow hydrogenation rates [228].

The reduction of aromatic nitro compounds to the corresponding aniline with $NaBH_4$ catalyzed by nickel complexes of *o*-amino-thiophenol Schiff base derivatives **110** was studied [229].



R = H, Me, Ph

110

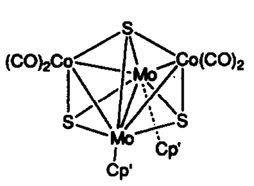
N-acylated anilides were prepared in good yields from nitroarenes in the presence of a carboxylic acid and methyl formate and catalytic amounts of $Ru_3(CO)_{12}$ at 180°C [130]. Homogeneous hydrogenations of 2-nitro-1-butanol to 2-amino-1-butanol and of 2-nitro-1-phenylpropane to amphetamine catalyzed by group VIII transition metal phosphine complexes were described [231].

Heterogenized Pd^{II} chelates were used in catalytic hydrogenation of chloronitrobenzenes to chloroanilines (≤ 90% yields) [232]. Hydrogenation of chloronitrobenzenes using Pd^{II} chelates with alizarine S and RNHCMe=CHCOMe (R = Ph, $1/2CH_2CH_2$) deposited on sibunit afforded the corresponding anilines in EtOH or DMF with ≤ 100% selectivity [233].

Catalytic activities of Pd complexes with bi- and tridentate salicylaldimines containing sterically hindered phenol groups for $PhNO_2$ hydrogenation in homogeneous media were reported. Catalytic activity depends on the nature of the solvent and on the type of peripheral ligand substitution [234].

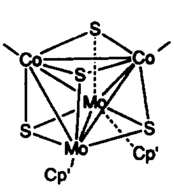
3.8. Miscellaneous hydrogenations

Thiophene and thiophenol were desulfurized by the sulfido-cobalt-molybdenum cluster **111** at 110–150°C and 15 bar H_2 pressure giving quantitatively **112** and hydrocarbons [235].



Cp' = MeC_5H_4

111



112

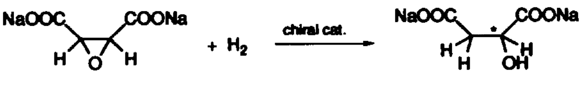
The hydrogenation of unsaturated fatty acid methylesters using a Ziegler-type catalyst containing Ni stearate and Et_3Al was studied with respect to the isomer distribution during hydrogenation [236].

The P=C double bond in **113** was hydrogenated at 25°C and 8 bar H_2 pressure in the presence of the covalent $Rh(Ph_2PCH_2CH_2PPh_2)Cl$ complex as the catalyst.

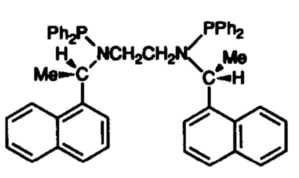
113 71%

Experiments with D_2 in place of H_2 indicated that there is a clean *cis* addition of D_2 to the double bond [237].

Asymmetric hydrogenolysis of **114** to give **115** in the presence of a chiral Rh catalyst was reported. The best result (62% ee) was obtained with [Rh(NBD)-(npepnnp)]BF_4 as catalyst at 25°C and 5 bar H_2 pressure (npepnnp = **116**). Deuterium labelling study has revealed that the epoxide hydrogenolysis proceeds *via* a direct C–O bond cleavage instead of an epoxide to ketone isomerization followed by ketone or enol hydrogenation [238].



114 **115**



116

Optimum reaction conditions were developed for the homogeneous catalytic hydrogenation of nitrile rubber, carboxylated nitrile rubber, and polybutadiene rubber with $RhCl(PPh_3)_3$. In the case of nitrile rubber in chlorobenzene at a catalyst concentration of 0.02 mmol, under 56 bar H_2 pressure at 100°C for 11h, was found to be optimum for complete hydrogenation [239].

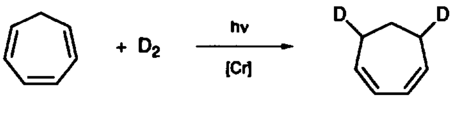
Esters were prepared in 52–85% yields by $(Ph_3P)_3$-Ru(H)Cl- or $(Ph_3P)_3RuCl_2$-catalyzed sequential Rosemund-Tishchenko reaction of acid chlorides with H_2 in the presence of 2,4,6-collidine [240].

$$2PhCOCl + 2H_2 \xrightarrow[55°C]{[Ru]} PhCOOCH_2Ph + 2HCl$$

85%

The hydrogenolysis of chloroarenes under biphasic or under phase-transfer conditions catalyzed by $L_2Rh(H)Cl_2$ ($L = P(^cHx)_3$, P^iPr_3) complexes was reported to proceed under mild conditions and to afford products in high yields. Functional groups such as R, OR, CF_3, COAr, COOH, and NH_2 are compatible with the carbon–chlorine bond cleavage process [241].

Photocatalytic hydrogenation of 1,3,5-cycloheptatriene in the presence of $(\eta^6\text{-cycloheptatriene})Cr(CO)_3$ afforded 1,3-cycloheptadiene. 1,6-Addition of dihydrogen was demonstrated by using D_2 [242].



3.9. Dehydrogenation

Mixtures of water with ethanol or methanol containing copper(II) sulfate were found to liberate dihydrogen upon UV irradiation [243]. Iron(III) chlorocomplex ions were found to generate H_2 from aqueous solutions of aliphatic alcohols on photolysis with a medium pressure Hg lamp at 26°C [244]. Ethanol was decarbonylated under remarkably mild conditions by $RuH_4(PPh_3)_3$ in a quantitative and irreversible reaction [245].

$$RuH_4(PPh_3)_3 + EtOH \xrightarrow{25°C} RuH_2(CO)(PPh_3)_3 + CH_4 + 2H_2$$

Cyclooctane and cycloheptane were catalytically dehydrogenated to cyclooctene and cycloheptene, respectively, with $RhCl(CH_2{=}CH_2)(PMe_3)_2$ at 70°C under visible light irradiation in the presence of ethene (1 bar) as hydrogen acceptor [246].

The mechanism of dehydrogenation of 2-propanol catalyzed by *trans*-$[IrClH(SnCl_3)_4]^{3-}$ or by *trans*-$[IrCl_2(SnCl_3)_4]^{3-}$ was investigated. Based on kinetic and isotope labelling experiments the predissociation of one $SnCl_3^-$ ligand and the rate-determining elimination of methine hydrogen has been suggested [247].

The dehydrogenation of cyclohexene and 1,3-cyclohexadiene to benzene and H_2 with a series of soluble tin(II)-coordinated platinum(II) complexes (*cis*-$[PtCl_2(SnCl_3)_2]^{2-}$, $[Pt(SnCl_3)_4]^{2-}$, $[Pt(SnCl_3)_5]^{3-}$ has been investigated under thermal condition [248].

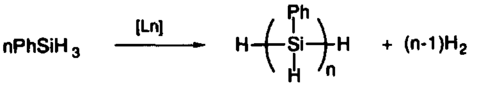
Catalytic dehydrogenative coupling of secondary silanes to disilane and short-chain oligosilanes has been achieved with the combination of Cp_2ZrCl_2 and 2 equiv of ^nBuLi in toluene at 90°C [249].

Dehydrogenation of methanol to H_2 has been achieved under reflux conditions in the presence of a catalytic amount of $RuCl_3 \cdot 3H_2O$ and an excess of sodium methoxide [250].

Photoenhancement of catalytic activity of *trans*-$[IrCl_2(SnCl_3)_4]^{3-}$ or $[IrH(SnCl_3)_5]^{3-}$ was observed for the dehydrogenation of 2-propanol at room temperature [251].

The ruthenium silyl complex was found to catalyze the coupling of $HSiMe_3$ at 150°C in cyclohexane to generate H_2 and oligomeric carbosilanes [252].

Dehydrogenative coupling of Si–H and N–H bonds to form small silazane oligomers was promoted by several dppm-bridged binuclear rhodium complexes. In the reaction of $PhSiH_3$ and RNH_2 with $Rh_2H_2(CO)_2(dppm)_2$, linear coupling silazane products were formed when $R = {}^iBu$, whereas branched coupling products were observed for R = H, Me [253]. Rapid dehydrogenative oligomerization of $PhSiH_3$ was observed in the presence of organolanthanide complexes of the type Cp'_2LnR (Ln = La, Nd, Sm, Y, Lu; R = H, $CH(SiMe_3)_2$), η^5-$(Me_2SiC_5Me_4)NdCH(SiMe_3)_2$, Cp'_2Sm, and $Cp'_2Sm(THF)_2$ at room temperature [254].



$$nPhSiH_3 \xrightarrow{[Ln]} H\left(\overset{Ph}{\underset{H}{Si}}\right)_n H + (n-1)H_2$$

Dehydrogenative aromatization of α,β-unsaturated cyclohexanones was achieved at 0°C with an oxovanadium compound obtained from $VO(OEt)Cl_2$ and AgOTf or Me_3SiOTf [255].

Polysilanes were formed in a $Cp_2NdCH(SiMe_3)_2$ catalyzed dehydrogenative condensation of trihydrosilanes at 80°C [256].

Dehydrogenation of cyclooctane catalyzed by $RhCl(CH_2{=}CH_2)(PMe_3)_2$ under ethene pressure at 170°C gave cyclooctene [257].

Oxidative dehydrogenation of cyclohexene to benzene at 50°C and 1 bar O_2 was catalyzed by $PdCl_2$ and anthraquinone-2-sulfonate as an electron-transfer reagent [258].

Active carbon supported $Na_5PMo_2V_2O_{40}$ was found to be an effective and selective catalyst for the aerobic oxidative dehydrogenation of alcohols and amines [259]. The effect of protonation in the photochemical dehydrogenation of alkanes (cyclooctane, cyclohexane, *cis*-1,2-dimethylcyclohexane and 2,3-dimethylpentane) with decatungstate ($W_{10}O_{32}^{4-}$) in CH_3CN was examined. Among others the protonation increases the quantum yields for alkane photooxidation by factors up to 25-fold [260]. The catalytic behavior of $H_6P_2W_{18}O_{62}$ was studied and compared with $H_2PW_{12}O_{40}$ in the oxidative dehydrogenation of ethylbenzene to styrene [261].

The photocatalytic dehydrogenation of pentane in the presence of $RhCl(CO)(PR_3)_2$ (R = Me, ${}^iPr$, Bu) was studied. Activity of these complexes with respect to dehydrogenation of pentane, ratio of 1-pentene/2-pentene, and photostability of the complexes changed in the order $Me \gg {}^iPr > Bu$ [262]. The wavelength dependence of photocatalytic cyclohexane dehydrogenation by $RhCl(CO)(PPh_3)_2$ and $RhCl(CS)(PPh_3)_2$ was interpreted in terms of the molecule orbital energy levels and orbital interactions [263].

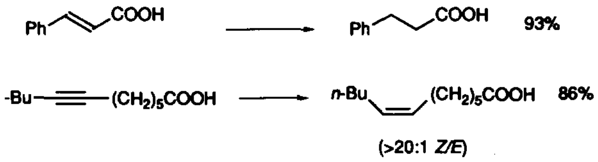
The oxidative dehydrogenation of isobutyric acid to methacrylic acid was studied over a series of 12-heteropolyoxometalate catalysts, $M_3PMo_{12}O_{40}$ (M = H, Cs, NH_4) [264]. See also [132].

3.10. Hydrogen transfer reactions (organic compounds as reductants)

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

Catalytic transfer-hydrogenation of α,β-unsaturated carboxylic acids in water or in a two-phase system using sodium or potassium formate as the hydrogen donor and *in situ* prepared rhodium complexes with sulfonated phosphines as the catalyst was reported. With chiral tetrasulfonated cyclobutanediop as the ligand, enantioselectivities up to 43% were obtained [265].

Treatment of water-soluble alkenes or alkynes with palladium(II) acetate and $(EtO)_3SiH$ at room temperature afforded the corresponding hydrogenated products in high yields [266]. *E.g.*:



Hydrogen transfer from HCO_2H/Et_3N (5 : 2) azeotrope to α,β-unsaturated carboxylic acids in the presence of chiral ruthenium-DIOP complexes as the catalyst gave the saturated carboxylic acids in up to 93% ee [267].

Diphenylacetylene was reduced into a 1 : 2 mixture of *E*- and *Z*-stilbene by polymethylhydrosilane in the presence of the ion pair $[(C_8H_{17})_3NMe]^+[RhCl_4(H_2O)_2]^-$ as the hydrogen transfer catalyst. The influence of the nature of the hydrogen donor, the acetylenic acceptor, and the catalyst system on the selectivity and efficiency of the transfer hydrogenation process has been investigated [268]. See also [134].

3.10.2. Transfer hydrogenation of ketones and aldehydes

Experimental evidence for the hydrogen-transfer mechanism from alcohols to ketones was provided by ^1H NMR spectroscopic identification of the intermediates **117**, **118** and **119** [269].

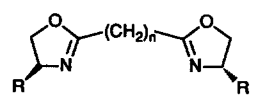
$$\underset{\mathbf{117}}{OsHL_4} + (CD_3)_2CO \rightleftharpoons \underset{\mathbf{118}}{OsHL_4(\eta_2\text{-}(CD_3)_2CO)} \rightleftharpoons \underset{\mathbf{119}}{OsL_4(OCH(CD_3)_2)}$$

$$L_4 = Cl(CO)(P^iPr_3)_2$$

An efficient transfer hydrogenation of both aliphatic and aromatic ketones by isopropanol in the presence of $RuCl_2(PPh_3)_3$ as the catalyst and NaOH as the cocatalyst was reported. Up to 900 turnovers per hour at 82°C were found in the case of cyclohexanone reduction [270].

Catalytic transfer hydrogenation of cyclohexanone in refluxing 2-propanol by complexes formed *in situ* from $Rh_2(OAc)_4$ and 1,4-benzodiazepines as the catalysts was studied [271]. The catalytic activity in the hydrogen transfer reduction of cyclohexanone with 2-propanol of immobilized $Rh_2(OAc)_4$ on γ-aminopropylated silica gel or styrene-divinylbenzene copolymer containing 3(5)-methylpyrazole groups was studied [272].

Transfer hydrogenations of aryl alkyl ketones with ^{i}PrOH in the presence of iridium(I) complexes of the ligand **120** as the catalyst were studied. Up to 91% ee was reported [273].



n = 0, 1; R = Ph, Me_2CH, (*S*)-EtCHMe

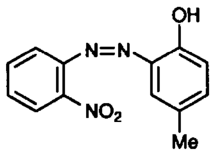
120

The transfer hydrogenations of cyclic and noncyclic ketones in the presence of $IrH_5(P^iPr_3)_2$, $RuH_4(PPh_3)_3$, and $ReH_7(P^iPr_3)_2$ complexes as the catalyst were studied [274].

3.10.3. Transfer hydrogenation of miscellaneous organic compounds

The $Ru_3(CO)_{12}$ + KOAc system catalyzes the the reduction of nitrobenzene by $HCO_2Et \cdot H_2O$ to aniline in EtOH and to a mixture of N-methyl-N-phenylformamide in HCO_2Et [90].

The reduction of the azo dye **121** and of indigocarmine with thiourea dioxide $[(H_2N)_2CSO]$ is catalyzed by $Co(dmg)_2$ [275].



121

Transfer hydrogenation of 3,3′-dinitro-4,4′-diaminodiphenyl ether at 70°C with hydrazine hydrate using Fe^{3+} as catalyst in MeOH as solvent gave 3,3′,4,4′-tetraminodiphenyl ether in 80% yield [276]. An intramolecular H_2 transfer has been recognized in lactone formation from O-allyl glucose by catalytic amount of $[(Ph_3P)_2RhCl]_2$ at 130°C in NMP [277].

3.11. Reduction without molecular hydrogen

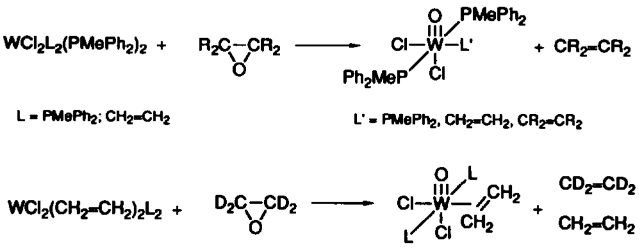
3.11.1. Stoichiometric reduction with low-valent transition metal complexes

The micellar effect of sodium dodecyl sulfate (SDS) on the reaction between Fe^{3+} and hydroquinone (H_2Q) and on the reaction between Fe^{2+} and quinone (Q) has been determined. The reaction with hydroquinone is accelerated, while the reaction with quinone is inhibited by SDS [278].

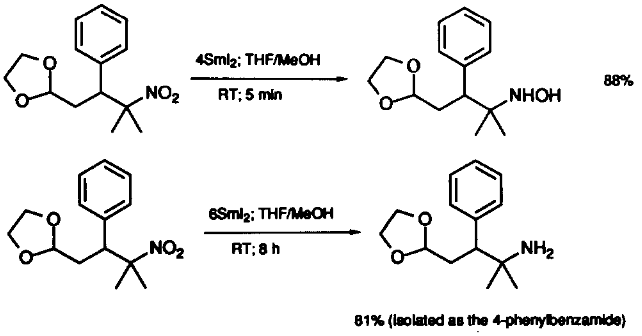
$$Fe^{3+} + H_2Q \rightleftharpoons Fe^{2+} + HQ + H^+$$

$$Fe^{3+} + HQ \rightleftharpoons Fe^{2+} + Q + H^+$$

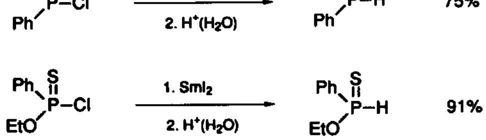
The mechanisms of the deoxygenation of epoxides by $WCl_2(PMePh_2)_4$ and $WCl_2(CH_2{=}CH_2)_2(PMePh_2)_2$ in the reactions below were studied. A concerted oxygen transfer to tungsten or a mechanism involving a short-lived radical intermediate was proposed [279].



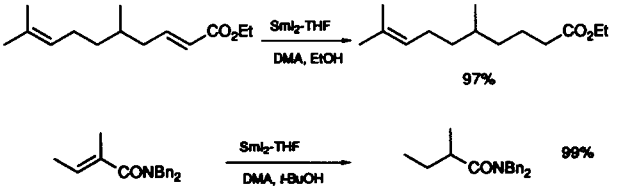
Alkyl hydroxylamines and alkyl amines have been prepared in moderate to good yields from primary, secondary, or tertiary nitroalkanes and SmI_2 at room temperature in the presence of methanol as a proton source [280]. *E.g.*:



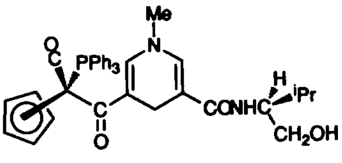
Certain P–Cl compounds were smoothly converted into the corresponding P–H compound at room temperature by SmI_2 [281]:



Ester, anhydride, amide, oxime, and carbonyl compounds were reduced to the corresponding alcohol as the major product (up to 81% isolated yield) with SmI_2 in the presence of $LiNH_2$, LiOMe or KOH at room temperature [282]. α,β-Unsaturated esters and amides were selectively reduced to the corresponding saturated ones at room temperature without affecting coexisting isolated double or triole bonds by using the reduction system, SmI_2 + N,N-dimethylacetamide + proton source [283]. *E.g.*:



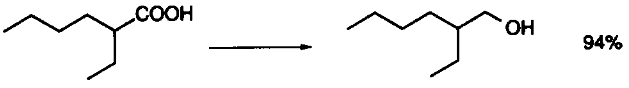
The NADH mimics homochiral complexes (*e.g.*: **122**) incorporating the chiral auxiliary $CpFe(CO)(PPh_3)$ at C-3 and a chiral β-hydroxycarboxamide, derived from valinol, at C-5 reduce ethyl benzoylformate to ethyl mandelate in greater than 97% ee [284].



122

Carboxylic acids were reduced to the corresponding alcohols in good yields by SmI_2 at room temperature [285]. *E.g.*:

$PhCOOH \longrightarrow PhCH_2OH$ 91%

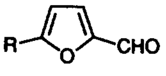


Nitroarenes were reduced to azo compounds by Cp_2TiCl in moderate yield. Benzylic and allylic chlorides and vicinal dibromides were catalytically transformed to the corresponding coupling products and alkenes by the Cp_2TiCl_2 + Al system [286].

$RuH_2(OOCCF_3)_2(P^cHx_3)_2$ was found to react instantly with cyclooctene to yield cyclooctane and $[Ru(C_6H_9P^cHx_2)(OOCCF_3)]_2(\mu\text{-}OOCCF_3)(\mu\text{-}OH_2)$ [287].

3.11.2. *Inorganic reductants in the presence of transition metal complexes*

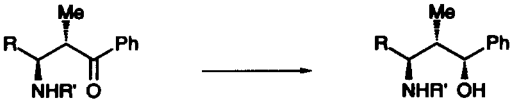
The furanoid aldehydes (**123**), benzaldehyde, and 2-thienylaldehyde were reduced to the corresponding alcohols with over 95% yields with HCOOH in toluene at 90°C using $Rh(PPh_3)_3Cl$ as catalyst. The rate of reduction decreased in the stated order of R; R = 3- or 4-pyridyl were inert under these conditions [288].



R = H, Me, HCO, Br, Me_3Si, Me_3Ge

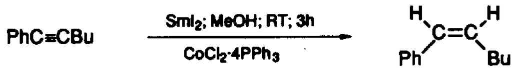
123

Triarylvinyl halides and acetates were reduced with $LiAlH_4$ using various transition metal chlorides as catalysts the vinylic halides were reduced to the corresponding alkenes while the vinylic acetates were reduced to mixtures of triaryl ketones and alcohols [289]. Reduction of the 1,3-aminoketones (**124**; R = Ph, ^{c}Hx, p-MeC_6H_4; R′ = H, COR; R = Me, OEt, Ph, p-ClC_6H_4, p-tolyl-, p-$MeOC_6H_4$) with $LiAlH_4$ in CH_2Cl_2 in the presence of $TiCl_4$, followed by base hydrolysis and a second reduction with $LiAlH_4$ gave the 1,3-aminoalcohols (**125**) with 80–95% yield [290].



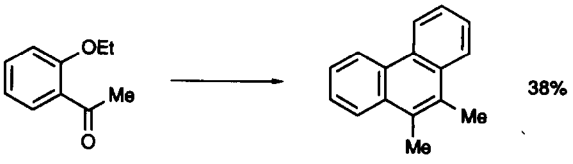
The catalytic reduction of nitrobenzene to aniline by the (TPP)FeCl + $NaBH_4$ system in diglyme at 30°C under dinitrogen atmosphere gave near 100% yield and 1700 turnover numbers [291]. α,β-Unsaturated carboxylic esters and amides were enantioselectively reduced with $NaBH_4$ in the presence of (semicorrinato)cobalt complexes as catalysts giving the corresponding saturated esters and amides with up to 98% ee [292].

Alkynes were selectively reduced to *cis*-olefins at room temperature by SmI_2 in the presence of $FeCl_3 \cdot 4PPh_3$, $CoCl_2 \cdot 4PPh_3$, or $NiCl_2 \cdot 4PPh_3$ catalysts and appropriate proton donors [293]. *E.g.*:

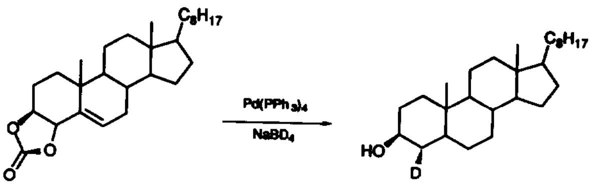


97% yield; >99% (*Z*)

Reductive deoxygenation and reductive dealkoxylation of alkoxy aromatic aldehydes and ketones afforded phenanthrenes in a one-pot synthesis using $TiCl_3$, Li and THF [294]. *E.g.*:

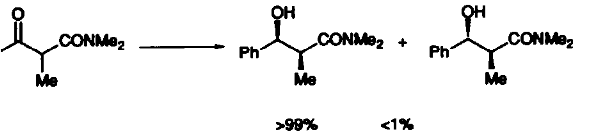


Palladium(0)-mediated borodeuteride reduction of **126** provided **127** in 58% yield [295].



126 **127**

In the presence of catalytic amounts of $MnCl_2$ the $NaBH_4$ reduction of 3-keto esters or 3-keto amides afforded *erythro*-3-hydroxy-2-methylpropionates or *erythro*-3-hydroxy-2-methylpropionamides, respectively [296]. *E.g.*:



Styrene was reduced to ethylbenzene by $NaBH_4$ at ambient temperature under dinitrogen in the presence of 5,10,15,20-tetrakis(*para*-substituted phenyl)-porphyrinatoiron(III) chloride complexes as the catalyst in alcohol. A s-alkyliron(III) porphyrin complex was assumed as intermediate in the reaction [297].

The $TiCl_3 + Zn(Cu) + Bu_3SnH$ reagent system in dry benzene was used to reduce $PrCHMeCO(CH_2)_3CHO$, PhCHO, and heptanal to the corresponding primary alcohol in 45–80% yield [298].

The mild and efficient deoxygenation of sulfoxides with titanium(IV) chloride + sodium iodide reagent system was reported. *E.g.*: $PhCH_2SOPh$ gave 95% yield of $PhCH_2SPh$ when treated with $TiCl_4 + NaI$ in MeCN at room temperature [299].

The reduction of cyclic acetals and ketals with $CpTiCl_3 + LiAlH_4$ in Et_2O at 30°C afforded the corresponding hydroxyethyl ethers and hydrocarbons [300]. Aromatic nitro compounds were reduced to the corresponding amines in good yields by borohydride exchange resin in the presence of transition metal (Pd, Co, Ni, Cu) compounds as catalysts [301]. See also [286].

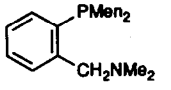
3.11.3. Reduction via hydrosilylation

A catalytic hydrosilylation system prepared from titanocene dichloride and ${}^{n}BuLi$ was developed for the conversion of esters to primary alcohols, which utilizes inexpensive silanes such as $HSi(OEt)_3$ as the stoichiometric reductant. Ethyl 6-bromohexanoate was cleanly converted to 6-bromo-1-hexanol (78% isolated yield). Likewise, α,β-unsaturated esters and esters containing phenolic, amino, or cyclopropyl groups were efficiently transformed into the corresponding alcohols [302].

$RhCl(PPh_3)_3$ was found to be an effective catalyst for the homogeneous reductive silylation of quinones with triethylsilane at 80°C in benzene solution [303].

The asymmetric hydrosilylation of acetophenone with diphenylsilane at room temperature under atmospheric pressure of H_2 using **128-130** as ligands and $[Rh(COD)Cl]_2$ as catalyst precursor gave (*R*)-1-phenylethanol with up to 21% ee [304].

128



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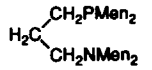
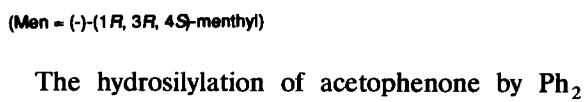


130

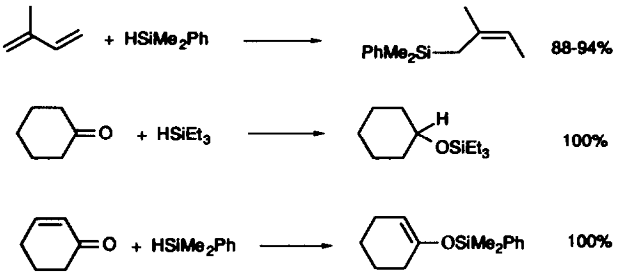
(Men = (-)-(1*R*, 3*R*, 4*S*)-menthyl)

The hydrosilylation of acetophenone by Ph_2SiH_2 was catalyzed with $CpFe(CO)_2Me$ and with $CpFe(CO)(SiHPh_2)_2$ [305].

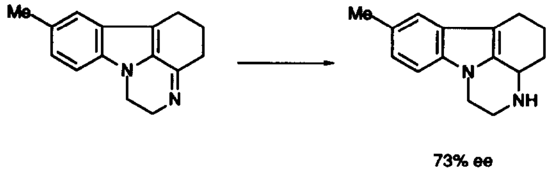
Hydrosilylation of the C=O functional group in various acyl-transition-metal complexes with Ph_2SiH_2 in the presence of a catalytic amount of $RhCl(PPh_3)_2$ leads to the formation of the corresponding α-silyloxy alkyl complexes [306,307]. Acylmanganese pentacarbonyls were found to be extremely efficient aldehyde and ketone hydrosilylation catalysts. A 1:1 mixture of aldehyde and hydrosilane gave quantitatively the corresponding silyl ether in the presence of 2–4% of $(CO)_5MnC(=O)R$ (R = Me or Ph) [308]. The manganese acyl complexes $L(CO)_4MnC(=O)R$ (L = CO, PPh_3, PEt_3,; R = Ph, Me) were found to be effective catalysts for the hydrosilylation of $Fe(CO)_2(\eta^5\text{-}C_5H_5)\text{-}C(=O)R$ (R = Me, Ph) compounds with monohydro-, dihydro, and trihydrosilanes [309]. *E.g.*:

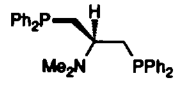


Hydrosilylations of isoprene, cyclohexanone, and cyclohexenone were catalyzed by $Rh_4(CO)_{12}$, $Co_2Rh_2(CO)_{12}$, and $Co_3Rh(CO)_{12}$ [310]. *E.g.*:



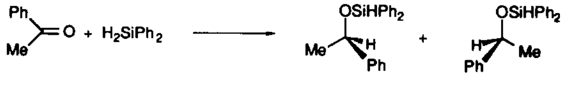
Asymmetric hydrosilylation of imines and oximes using $[Rh(COD)Cl]_2 + (\mathbf{131})$ catalyst gave the corresponding amines in moderate to high optical purity [311]. *E.g.*:





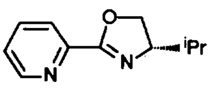
131

Asymmetric hydrosilylation of acetophenone with Ph_2SiH_2 using *in situ* Co^I + pyridinyloxazoline catalyst gave 52.9–56.3% ee of (*R*)-**132** in the best case with **133** as cocatalyst [312].



(*R*)-**132** (*S*)-**132**

The enantioselective hydrosilylation of acetophenone by Ph_2SiH_2 using $[Rh(COD)Cl]_2$ and pyridineoxazolines **134** as the catalyst was investigated. The substitution of H in the 6-position of the pyridine ring reduces the dependence of the optical induction on ligand excess, solvent, and concentration of Ph_2SiH_2, acetophenone, and rhodium. The 6-substituents on the pyridine ring are assumed to block one of the coordination sites of rhodium, preventing further interaction with additional ligands, solvents, substrates, and additives [313]. In the enatioselective hydrosilylation of acetophenone with Ph_2SiH_2 5.5–7.6% ee was obtained using an *in situ* catalyst from $[Rh(COD)Cl]_2$ and **135** or **136** [314].



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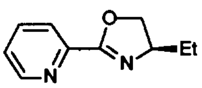

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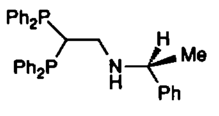

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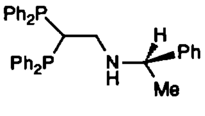
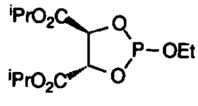


136

New chiral C_2-symmetric bioxalines and bithiazolines as ligands in the rhodium(I)-catalyzed asymmetric hydrosilylation of acetophenone induced up to 84% ee [315]. μ-Dichlorodirhodium complexes with chiral phosphites such as **137** were found to catalyze the asymmetric hydrosilylation of acetophenone with Ph_2SiH_2 giving the maximum optical yield of 24% [316].



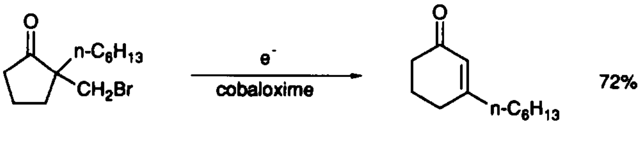
137

The asymmetric hydrosilylation of acetophenone using Rh^I complexes with aminopyridine-based chiral, bidentate ligands gave enantioselectivities between 4 and 42%. Electron-withdrawing substituents on the pyridine ring gave the better results [317]. Complexes obtained from $[Rh(COD)Cl]_2$ and (*S*)-$PhCH_2CH(NMe_2)CH_2PPh_2$ or (*S*)-2-$Ph_2PC_6H_4CH(NMe_2)Me$ were used in asymmetric hydrosilylation of acetophenone by Ph_2SiH_2 [318].

3.11.4. Electroreduction and photoreduction

Electrochemical reduction of CO_2 to CO and formate in the presence of Ru bypyridine and phenathroline complexes was studied in MeCN-water, MeOH, and MeCN-MeOH solutions [319]. Titanium dioxide coated with Fe^{2+}- or Co^{2+}-phthalocyanine catalyze the reduction of carbonate under irradiation with a low-pressure mercury lamp. Formate, formaldehyde, and methanol are formed, their yield increasing in the stated order. Methanol is the main product probably because the other two organic compounds are also reduced under the applied conditions [320]. The complex *cis*-$[Ru(bpy)_2(CO)H]^+$ was found to be a catalyst for the electrochemical reduction of CO_2 to formate ion in MeCN-water. Cyclic voltametric and controlled potential electrolysis studies have shown that the key steps in this electrocatalyzed reduction are the reductively induced insertion of CO_2 into the Ru–H bond and the re-formation of the metal hydride by the reduction of water [321].

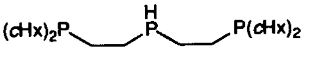
A cobaloxime-mediated indirect electroreduction of **138** to form **139** was reported [322].



138 **139**

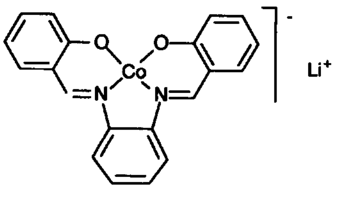
The incorporation of CO_2 into nonactivated mono- and disubstituted alkynes catalyzed by electrogenerated nickel-bipyridine complexes afforded α,β-unsaturated carboxylic acids in moderate to good yields [323].

The electrochemical reduction of CO_2 to CO catalyzed by iron(0) porphyrins was studied [324]. The electrochemical reduction of CO_2 to CO in acidic DMF or acetonitrile solution was catalyzed by [Pd(triphosphine)(solvent)](BF$_4$)$_2$ complexes. Using the triphosphine ligand **140**, 85% current efficiency and 130 turnovers were achieved. The kinetics of the reaction were studied [325].



140

The electrochemical reduction of CO$_2$ to CO and CO$_3^{2-}$, in MeCN containing LiClO$_4$ as a supporting electrolyte, was catalyzed by [Co^I(salophen)Li] **141** [326].



141

In the p-terphenyl-catalyzed photoreduction of CO$_2$ to CO the addition of Co^{3+}-cyclam as an electron mediator enhanced the efficiency of the reaction (cyclam = 1,4,8,11-tetra-azacyclotetradecane) [327].

Polypyrrole films covalently substituted by polypyridyl Rh^{III} complexes were found to mediate the electrocatalytic hydrogenation of cyclohexanone [328].

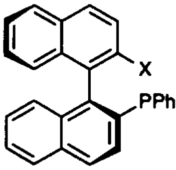
Polyphthalocyanine thin films modified with 2,4-diaminonitrobenzene followed by the reduction of nitro groups were used as an electrode for the enantioselective reduction of acetophenone after additional modification with aminoacids. In the case of L-phenylalanine, (S)-(−)-1-phenylethanol was produced in up to 19.1% ee [329].

3.12. Hydrosilylation, hydrogermylation, and hydrostannation

OsHCl(CO)(P^{i}Pr$_3$)$_2$ was found to be a very active and highly selective catalyst for the addition of triethylsilane to phenylacetylene to obtain *trans*- and *cis*-PhCH=CH(SiEt$_3$) [330].

The hydrosilylation of alkynes and alkenes with (Me$_2$HSi)$_2$O in the presence of Rh(acac)(CO)$_2$ as the catalyst was studied. Reaction of HC≡CH afforded (CH$_2$=CHSiMe$_2$)$_2$O in quantitative yield [331]. Polymeric rhodium-carborane complexes were used as catalyst in the reaction of 1-hexene with Et$_3$SiH, which gave mixtures of Me(CH$_2$)$_3$CH=CHSiEt$_3$ and Me(CH$_2$)$_5$SiEt$_3$ in 31–92% overall yields [332]. Allylsilanes or vinylsilanes were formed in moderate to high isolated yields in the rhodium(II) perfluorobutyrate catalyzed hydrosilylation of 1-alkynes at 25°C, depending on the mode of addition of the reactant [333]. The complex (triso)Ir(C$_2$H$_4$)$_2$ (triso = C(Ph$_2$P=O)$_3$) has been found to catalyze the dehydrogenative silylation and hydrosilylation of ethylene with triphenylsilane and diphenylmethylsilane in CH$_2$Cl$_2$ solution at 25°C. The isolated complex (triso)Ir(SiPh$_3$)H(C$_2$H$_4$) seems to be an intermediate in ethene hydrosilylation [334].

Nickel acetylacetonate was found to be a catalyst of the reaction of vinyltriethoxysilane and triethoxysilane to give bis(silyl)ethane and bis(silyl)butanes as the main products at 120°C [335]. Optically active 2-alkanols (> 94% ee) were prepared from alkyl-substituted terminal olefins such as 1-hexene and 1-octene *via* [PdCl(π-C$_3$H$_5$)]$_2$ + (S)-MOP-catalyzed hydrosilylation ((S)-MOP = **142**) followed by oxidation of the carbon–silicon bond [336].

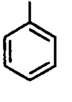


X = OMe, O^{i}Pr, OCH$_2$Ph, Et

142

The hydrosilylation of 1,5-hexadiene with Et$_3$SiH and Me$_2$SiOCHMe$_2$H in the presence of Rh(CO)$_2$(acac) or H$_2$PtCl$_6$ as the catalyst was studied [337]. Reactions of CH$_2$=CH(CH$_2$)$_n$CH$_3$ (n = 3-15) with ≡Si–H groups on the surface silica in the presence of H$_2$PtCl$_6$ gave silica-bound ≡Si–CH$_2$CH$_2$(CH$_2$)$_n$CH$_3$ silyl alkanes [338]. Hydrosilylation of 1-hexene and of styrene by H$_8$Si$_8$O$_{12}$ catalyzed by H$_2$PtCl$_6$ gave the corresponding C$_6$H$_{13}$Si$_8$H$_7$O$_{12}$ molecules in 15–20% isolated yield [339]. The effect of phosphine-ligand structure on catalytic properties of *cis*- and *trans*-Pt(PR$_3$)$_2$Cl$_2$ (*e.g.*: R = Ph, Et, Bu, ^{i}Pr) and other complexes in the 1-heptene hydrosilylation with MeSiHCl$_2$ was studied. The catalytic activity decreased with increasing electron-donating properties and size of the phosphine ligands [340]. The effect of phosphine ligand structure in platinum(II) complexes on their catalytic properties in hydro-silylation was studied. Thus, the catalytic activity of bis(phosphine)-platinum com-plexes for hydrosilylation of 1-heptene with MeSiHCl$_2$ decreased with increasing elec-tron-donor properties of the phosphine and increasing size of its substituents [341].

The kinetics of the platinum-catalyzed hydrosilylation of **143** and **144** with **145** using dichloro(dicyclopentadiene)platinum(II) as catalyst precursor were studied [342].



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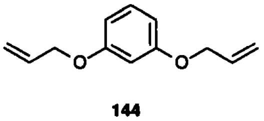

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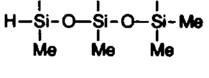
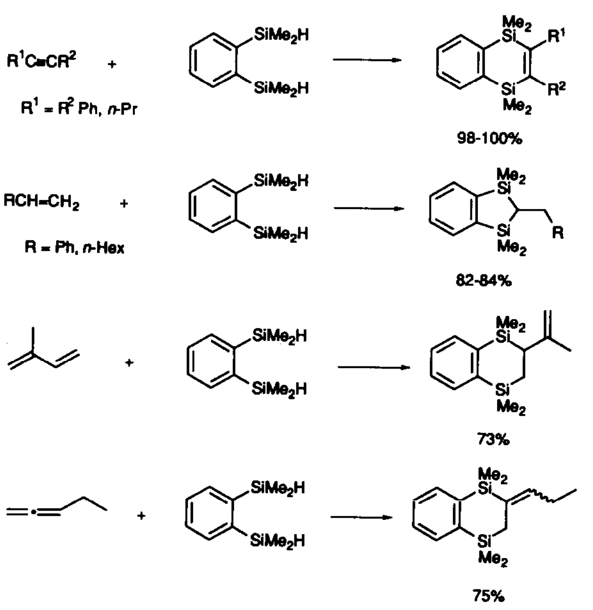


$$\mathrm{H{-}\underset{Me}{\overset{Me}{Si}}{-}O{-}\underset{Me}{\overset{Me}{Si}}{-}O{-}\underset{Me}{\overset{Me}{Si}}{-}Me}$$

145

Hydrosilylation of α,β-unsaturated esters and other vinyl- and vinylidene type olefins was studied using $PtCl_2(PhCN)_2$, $RhCl(PPh_3)_3$ and various platinum-phosphine catalysts [343]. Hydrosilylation of 1-hexene and 1,5-hexadiene with SiH_4 in the presence of various transition metal complexes was studied. The highest product yield was obtained with $Pt(PPh_3)_4$ as catalyst [344]. Hydrosilylation of terminal alkynes with several Si–H compounds was investigated in the presence of highly active platinum(0) olefin catalysts [345].

A Pt-complex-catalyzed dehydrogenative double silylation of acetylenes, olefins and dienes was reported. $Pt(PPh_3)_2(CH_2{=}CH_2)$ was found to be the best catalyst in benzene solution [346]. Some examples:



$Pt(PPh_3)_2(CH_2{=}CH_2)$ was found to be a versatile catalyst in hydrosilylation of alkenes and functionalized alkenes [347].

Faster reactions and improved yields were obtained in hydrosilylation of 2-vinylpyridine or 4-vinylpyridine with methyldichlorosilane and CuCl using microwave energy [348].

The hydrosilylation of styrene, 1-hexene, and 2-pentene with H_2SiPh_2 was carried out at 25°C with catalysts generated from zirconocene dichloride and two equivalents of butyllithium [349]. Regioselective hydrosilylation of alkenes with H_2SiPh_2 was catalyzed with the product of the reaction of Cp_2ZrCl_2 and EtMgBr [350]. *E.g.*:

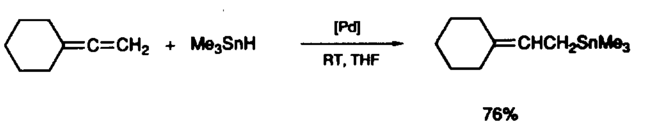
$$C_6H_{13}CH{=}CH_2 + H_2SiPh_2 \longrightarrow C_6H_{13}CH_2CH_2SiHPh_2$$

73% yield >99% regioselectivity

The hydrosilylation of alkenes (styrene, 1-decene, and 2-heptene) with di-or tri-hydrosilanes were effectively catalyzed at 30–80°C by $[(C_5Me_5)_2NdH]_2$ and $[(C_5Me_5)_2NdCH(SiMe_3)_2]$ in benzene solution [351].

Phenylacetylene was hydrosilylated or hydrogermylated with Bu_3SiH or Bu_3GeH in the presence of $Rh(L)(C_2H_4)_2$ (L = acac, $CF_3C({=}OCHC({=}O)CF_3)$) to produce $Ph(Bu_3M)C{=}CH_2$ (M = Si, Ge) selectively [352].

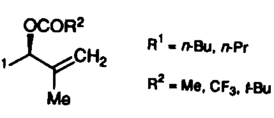
Reaction of allenic ethers with $HSnBu_3$ or $HSnPh_3$ in the presence of $Pd(PPh_3)_4$ gave allylstannanes in good yield [353]. In the $Pd(PPh_3)_4$-catalyzed hydrostannation of terminal allenes regioselective formation of allylstannanes were observed [354]. *E.g.*:



See also [112,155,208,306–310,312–318].

3.13. Hydroboration

The stereochemistry of the $[Rh(COD)Cl]_2 \cdot 2PPh_3$-mediated hydroboration of allylic alcohol derivatives **146** and methyleneadamantanes **147** with catecholborane was studied [355].



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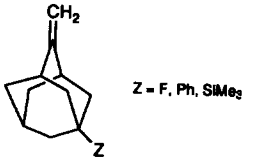
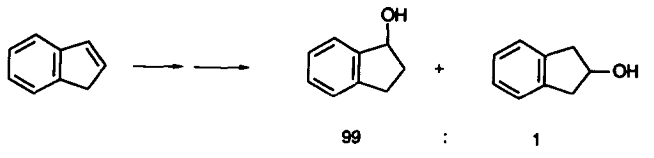


147

Reactions of deuteriocatecholborane with alkenes in the presence of $RhCl(PPh_3)_3$ were reinvestigated. It was concluded that labeling studies provide very little information concerning the mechanism(s) of rhodium-catalyzed hydroboration reactions either with commercial (aged) catalyst [356] or with freshly prepared one [357]. Enantioselective hydroborations of norbornene, indene, α-methylstyrene, and 2,3,3-trimethyl-1-butene with catecholboranes were performed *via* catalysis with rhodium complexes containing various chiral ligands. Thus, hydroboration of α-methylstyrene in the presence of $[Rh(COD)Cl]_2$ and (−)-DIOP gave (*R*)-$PhCHMeCH_2OH$ with 27% ee after oxidative workup [358].

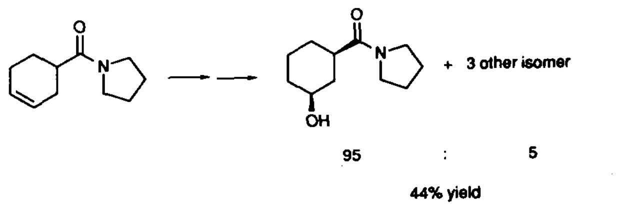
Asymmetric hydroboration of styrenes catalyzed by cationic (*R*)-BINAP-Rh^I complexes gave after oxidation optically active (*R*)-1-aryl-ethanols in high yields with up to 96% ee [359].

Hydroboration of vinylarenes with catecholborane or $BH_3 \cdot Me_2S$ in the presence of $RhCl(PPh_3)_3$ or $[Rh(COD)Cl]_2$ and PPh_3 gave the corresponding α-alcohols selectively after oxidation with H_2O_2 in high yields. *E.g.*:



With BINAP as chiral phosphine ligand in styrene or substituted styrene hydroborations enantiomeric excesses ranged between 91 and 96% [260].

Secondary amides were shown to effectively direct the $[Ir(COD)(P^{c}Hx_3)(py)]PF_6$-catalyzed hydroboration of olefins with catecholborane. Both cyclic and acyclic olefins were hydroborated with high levels of stereo- and regioselectivity. Oxidative workup resulted the corresponding alcohol in 44–82% yield [361]. *E.g.*:



The rhodium complex-catalyzed hydroboration of styrene with the cyclic secondary boranes derived from ephedrine and pseudoephedrine was investigated [362]. See also [617].

4. Oxidation

4.1. Catalytic oxidation of hydrocarbons and hydrocarbon groups with O_2

4.1.1. Oxidation of saturated hydrocarbons

Non-traditional mechanisms were discussed for catalytic oxidation of hydrocarbons with emphasis on alkane oxidation by metal complexes [363].

The binuclear iron complex $[\{Fe(HBpz_3)(hfacac)\}_2O]$ was found to be effective for dioxygen hydroxylation of alkanes (*e.g.*: pentane) and arenes (*e.g.*: benzene) in the presence of Hhfacac and Zn powder in CH_2Cl_2 at 25°C and 1 bar O_2 ($HBpz_3$ = hydrotris-1-pyrazolylborate, Hhfacac = hexafluoroacetylacetone) [364]. Oxidation reactions of cyclohexene, toluene, and adamantane with iron complexes, $Fe_2O(OAc)_2(bpy)_2Cl_2$, $Fe_4O_2(OAc)_7(bpy)_2ClO_4$, $Fe_2O(OAc)(tmima)_2(ClO_4)_3$ (tmima = tris[(1-methylimidazol-2-yl)methyl]amine) using $H_2O_2 + O_2$ as the oxidant were studied [365].

Several μ-oxo Fe^{III} complexes having porphyrinato, polyoxometalate, and silicometalate molecular environments were examined for catalytic activity in alkane oxidation in both liquid and vapor phase. The activity and selectivity of these catalysts depend upon the molecular environment of the μ-oxo species used as the catalyst precursor. In some instances *in situ* conversion of μ-oxo to ferryl oxo species was assumed to be the key to catalysts capable of direct hydroxylation of alkanes with air or oxygen [366].

The oxidation of alkanes using $FeCl_2 \cdot 4H_2O$, Zn, and O_2 in pyridine + acetic acid in the presence of trimethylphosphite afforded alkyl dimethyl phosphates [367]. The Gif family of systems for the selective oxidation of saturated hydrocarbons were briefly described. The mechanism of the reaction was analyzed based on the identified iron complex intermediates [368]. A product study of the side-chain oxidation of alkylbenzenes under Gif^{IV} conditions (Fe^{III}, py, AcOH, Zn, and O_2) has shown that only one of the two competing oxidation pathways require catalysis by Fe^{III}. The catalyzed pathway has been found particularly effective towards secondary positions [369]. Kinetic isotope effects were measured for oxidation of $c\text{-}C_6H_{12} + c\text{-}C_6D_{12}$ in pyridine for different Gif-type (Fe^{III}; Cu^{II}; O_2; H_2O_2) and Fenton ($Fe^{II} + H_2O_2$) systems [370]. A catalytic system composed of a μ-oxo binuclear iron(III) complex which is effective for dioxygen oxidation of alkanes was developed. This system mimics methane monooxygenase catalysis [371]. Saturated C–H bonds in cyclohexane and adamantane were monooxygenated with 1 bar O_2 to alcohols and ketones by $FeCl_3$ + pyrocatechol + hydroquinone + pyridine system in acetonitrile at 45°C [372].

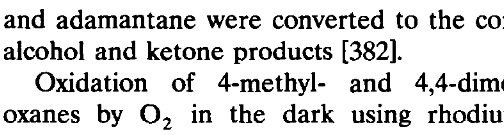
The selective oxygenation of cyclohexane to cyclohexanol and cyclohexanone at 30°C and atmospheric pressure was achieved with chlorotetraphenylporphyrinato-Mn^{III}, -Fe^{III}, or -Co^{II} complexes as catalyst and ascorbic acid as coreductant. The catalytic efficiency was found to be sensitive to the peripheral phenyl substitution pattern of the porphyrinato ring in the complexes. The following phenyl substituents were investigated: $(m,m',p\text{-OMe})_4$, $(m\text{-OMe}, p\text{-OH})_4$, $(o\text{-OMe})_4$, $(p\text{-Cl})_4$, $(p\text{-OMe})_4$, $(o\text{-OEt})_4$, $(o\text{-Br})_4$, $(p\text{-NO}_2)_4$, and $(m\text{-Cl})_4$. The $(m\text{-OMe}, p\text{-OH})_4$ substituents and Fe^{III} combination gave the relative highest oxygenation activity [373].

Selective catalytic oxidation of saturated hydrocarbons and alcohols was achieved by oxo ruthenium complexes. The complex $[Ru^{III}(EDTA)(H_2O)]^-$ catalyzes the oxidation of saturated hydrocarbons to alcohols and of alcohols to the corresponding aldehydes or ketones with O_2 or NaOCl as the oxidant [374].

The catalytic liquid-phase oxidation of 2,4-dichlorotoluene by O_2 in the presence of Co^{2+}, Mn^{2+}, or Zn^{2+} salts at 155°C was investigated. $Co(OAc)_2$ was found to be the most effective catalyst, which gave a 63–65% yield of 2,4-dichlorobenzoic acid [375]. Optimal conditions for oxidation of 2,4-dichlorotoluene to 2,4-dichlorobenzoic acid in the presence of Co^{2+}, Mn^{2+}, and Br^-, affording 98% product for 100% substrate conversion, were found to be 16 bar air pressure, 160°C, and AcOH as solvent [376]. The oxidation of **148** with O_2 (1 bar) catalyzed by tetra(4-chloro-phenyl)porphyrinatocobalt(II) in ethyl acetate solution at 25°C gave **149** selectively in 83% yield [377]. The mechanistic details of the reaction were discussed [378].

148 **149**

Ethane was oxidized with $Co(O_2CCF_3)_3$ or $O_2 + Co(O_2CCF_3)_3$ in trifluoroacetic acid solution at 130–200°C under pressure to form ethyl trifluoroacetate and 1,2-bistrifluoroacetoxyethane in successive reactions along with products of C–C bond cleavage. Propane gave similar oxidative reactions [379]. The effect of various cobalt salts on the benzoyl peroxide initiated oxidation of nonane with dioxygen was investigated [380]. In the presence of catalytic amount of cobalt(II) acetate, manganese(II) acetate and bromide ion, the oxidation of **150** with air (70 bar) at 130°C afforded **151** selectively in > 95% yield [381].

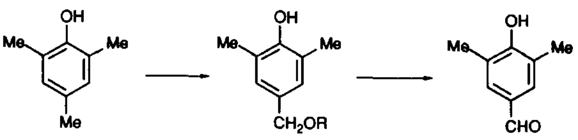


150 **151**

A weakly solvated cobalt-acetonitrile complex, $[Co(NCCH_3)_4](PF_6)_2$ was found to catalyze the air oxidation of alkanes at 75°C and 3 bar. Cyclohexene and adamantane were converted to the corresponding alcohol and ketone products [382].

Oxidation of 4-methyl- and 4,4-dimethyl-1,3-dioxanes by O_2 in the dark using rhodium carbonyl clusters and Cu complexes as catalysts gave 100% selectivity in the formation of the corresponding hydroperoxides. The photochemical oxidation of 4,4-dimethyl-1,3-dioxane in the presence of $Rh_6(CO)_{16}$ gave 60% selectivity in the formation of hydroperoxide [383]. Developments using Ru and Rh complexes in nonradical, coordination catalysis of various oxidations with O_2 or air were discussed [384].

4-Hydroxy-3,5-dimethylbenzaldehyde (**154**) was obtained in 87% yield by oxygenation of **152** in n-hexanol solution at 40°C in the presence of $CuCl_2 \cdot 2H_2O +$ acetoxime catalyst system. When the reaction was interrupted at 52% conversion, the ether **153** was obtained in 43% yield [385]. When acids were present, preferential formation of 2,6-dimethyl-*p*-benzoquinone was observed. A plausible mechanism of oxidation has been suggested [386].



152 **153** **154**

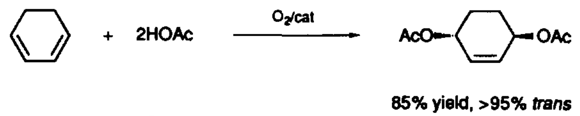
Silica gel, functionalized by (N,N-dimethyl-3-aminopropyl)trimethoxysilane and complexed with different M^{II} ions in the presence of O_2 was found to be effective for the aerobic, room temperature oxidation of cyclohexane to give cyclohexanol and cyclohexanone as the products. The order of reactivity is M = Cu > Fe ≈ Mn ≈ Ni ≈ Co [387].

4.1.2. Oxidation of olefins

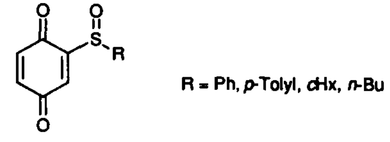
The oxygenation of 1-acetoxy-2-cyclohexene to allylic oxidation products and epoxide in the presence of $MO_2(acac)_2$, $VO(acac)_2$, Cr^{III}-stearate, and $Cr(acac)_3$ as catalyst was studied [388].

A quantitative catalytic oxygenation of styrene to 1-phenylethanol was obtained in the presence of an Fe^{III} complex of 5,10,15,20-tetrakis(1-methyl-4-pyridino)-porphine tetrachloride in water at pH 12 containing $NaBH_4$ [389].

The Wacker-oxidation of 1-decene to 2-decanone by O_2 catalyzed by $Pd(OAc)_2$, hydroquinone and iron(II) phthalocyanine in aqueous dimethylformamide gave high yields at room temperature [390]. The use of sulfinyl quinones **155** as cocatalysts in the triple catalytic system $Pd(OAc)_2$ + **155** + iron phthalocyanine + air + AcOH at 25°C improved the stereochemical outcome of the 1,4-diacetoxylation of 1,3-cyclohexadiene [391].

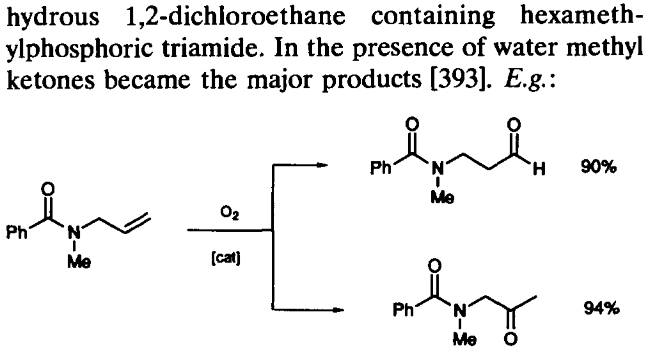


85% yield, >95% *trans*



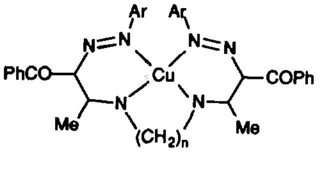
155

Oxidation of allylamine in acid solution with $PdCl_2 + CuCl_2 + O_2$ at 60°C gave 1-amino-propan-2-one in yields up to 42% [392]. Regioselective formation of aldehydes was observed from N-allylamides and lactames with molecular oxygen at room temperature in the presence of $PdCl_2(MeCN)_2$ + CuCl catalyst in anhydrous 1,2-dichloroethane containing hexamethylphosphoric triamide. In the presence of water methyl ketones became the major products [393]. *E.g.*:



The possible configurations of the Wacker process was investigated by using pseudopotential *ab initio* MO method. Four isomers of $PdCl_2(C_2H_4OH)_2$ were found by scanning the potential energy surface [394].

The relationship between redox potentials and catalytic activities of **156** in the liquid-phase oxidation of cyclohexene with O_2 was investigated [395].

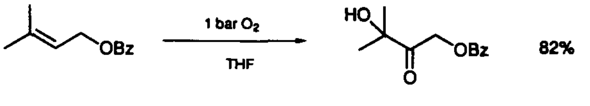


n = 2, 4

Ar = p-NO_2, p-Br

156

The Co(pc) + NO/NO_2 and Fe(pc) + NO/NO_2 (H_2pc = phthalocyanine) systems were studied with regard to their O_2 activation and oxygen-atom-transfer reactions, in the oxidation of terminal olefins to the corresponding methyl ketones [396]. The multistep nature of the aerobic oxidation of cyclohexene catalyzed by a series of aquo(phosphine)ruthenium(II) complexes was demonstrated from the correlation of catalyst turnovers with the rate constants of ligand substitution, and the correlation of catalyst turnovers with the Hammett s_p values [397]. Various olefinic compounds were directly converted into the corresponding α-hydroxy ketones in good yields with molecular oxygen and an aldehyde in the presence of the catalyst system of OsO_4 and bis(3-methyl-2,4-pentadionato)nickel(II) at room temperature [398]. *E.g.*:

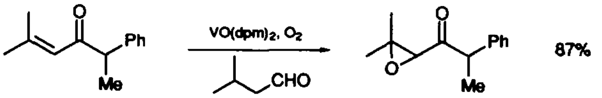


The mechanistic aspects of the catalytic oxygenation of cyclooctene in the presence of $\{RhCl(C_8H_{14})_2\}_2$ have been discussed [399].

4.1.3. Epoxidation of olefins

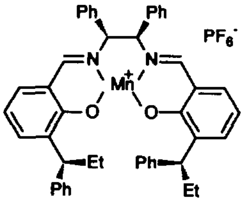
Applications of some β-ketophosphonate transition metal complexes in epoxidation catalysis were investigated [400].

The Sharpless epoxidation of allyl alcohols was applied as the first step in a multistep synthesis of chiral propargyl alcohols [401]. Epoxidation of α,β-unsaturated carboxamides with molecular oxygen and an aldehyde at 25°C in the presence of a catalytic amount of $VO(dpm)_2$ (Hdpm = ${}^tBuC(=O)CH_2C(=O){}^tBu$), gave the corresponding 2,3-epoxycarboxamides in good yields [402]. *E.g.*:



The oxomolybdenum(V) complexes of 5,10,15,20-tetrakis(3,5-di-t-butyl-phenyl)porphyrin and 5,10,15,20-tetrakis(*p*-tolyl)porphyrin were used as catalysts for the epoxidation of 2-hexene and 2-hexen-1-ol with O_2 under irradiation of a 500 W tungsten lamp. Catalytic turnovers between 3 and 75 were achieved [403]. New polydentate molybdenum(VI)-grafted poly(amido amine) resins were used as heterogeneous epoxidation catalysts [404]. Several sterol esters bearing various patterns of unsaturation were epoxidized by air using *trans*-$(TMP)Mo(=O)_2$ as catalyst. Usually a high degree of β-stereoselectivity was observed [405,406]. The epoxidation of isobutene-isoprene copolymer with H_2O_2 in the presence of methyltrioctylammonium tetrakis(diperoxotungsto)phosphate(3 −) as the catalyst in a biphasic system was studied. The optimum reaction temperature was found to be ~ 60°C [407].

The asymmetric epoxidation of alkenes catalyzed by chiral (salen)Mn^{III} complexes **157** and **158** was investigated. The highest asymmetric induction was obtained in the epoxidation of (*E*)-PhCH=CHMe (56% ee) and 1,2-di-hydronaphthalene (83% ee) [408].



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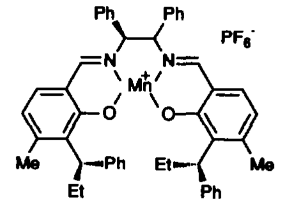


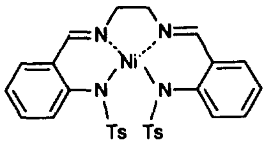
158

Sterically hindered Mn^{III} and Fe^{III} complexes of tetrakis(2,6-di-chlorophenylporphyrin) and tetrakis(2,4,6-trimethylphenylporphyrin) were applied as catalysts for epoxidation of propene by O_2 in the presence of propionaldehyde as reducing agent [409]. A wide variety of epoxides were prepared in good to quantitative yields by the aerobic oxidation of styrene analogous or olefinic alcohols by using tris(1,3-diketonato)iron(III) complexes, particularly tris(1,3-bis(*p*-methoxyphenyl-1,3-propanedionato]iron(III) as the catalyst at room temperature [410].

Oleic acid was epoxidized with O_2 in the presence of PhCHO using a Co-type ion-exchange membrane as catalyst with 86% selectivity. The epoxide was formed by a series of free radical reactions. No leakage of Co ions was observed [411].

Polyoxoanion-supported Rh, Ir, and Ru complexes were examined as catalyst precursors in cyclohexene epoxidation by O_2. The complex $[Bu_4N]_5Na_3(1,5\text{-COD}) \cdot IrP_2W_{15}Nb_3O_{62}$ showed the highest activity of this group with a turnover frequency of 2.9 h^{-1} at 38°C in CH_2Cl_2 which is 100-fold greater than that of its parent iridium compound, $[(1,5\text{-COD})IrCl]_2$ [412].

Complex **159** was found to be a good catalyst for the epoxidation of unfunctionalized olefins with molecular oxygen (1 bar) in the presence of 2-methylpropanol at 50°C in CH_2Cl_2 solution [413].



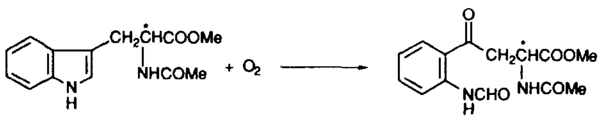
159

A highly efficient method was reported for the preparation of a variety of epoxides from trisubstituted, 1,2-disubstituted and terminal olefins using atmospheric pressure of oxygen as oxidant, an aldehyde as reductant and bis[1,3-bis(*p*-methoxyphenyl)-1,3-propanedionato]nickel(II) as catalyst at room temperature [414]. A potential cycle for olefin epoxidation using air as the oxidant was investigated. The proposed cycle comprised three steps: (a) epoxidation of an olefin using an organoplatinum hydroperoxide [Pt]OOH; (b) conversion of the resulting metal hydroxide [Pt]OH to the hydride [Pt]H using H_2 or an alcohol; and (c) reaction of the hydride [Pt]H with O_2 to generate the hydroperoxide. The feasibility of these steps were studied [415].

4.1.4. Oxidation of aromatics

The $[W_{10}O_{32}]^{4-}$-catalyzed aerobic photooxidation of alkyl-substituted benzenes at 25°C in MeCN solution was studied. High conversions (92–100%) and 90–91% yield of benzoic acid and *p*-toluic acid was observed from toluene and *p*-xylene, respectively. Acetophenone was formed from ethylbenzene in 71% yield. Cumene gave a mixture of acetophenone and 2-phenylpropan-2-ol in 76% yield [416].

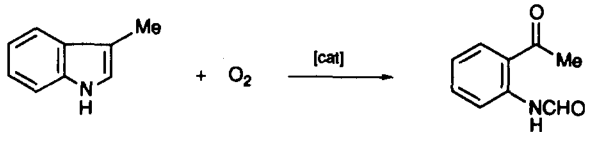
The oxidation of indole-3-acetic acid at 30°C in water in the presence of 1,10-phenanthroline-manganese complexes was studied [417]. Stereoselective dioxygenolyses of the pyrrole ring in N-acetyl-L-(+)- and D-(–)-tryptophan methyl esters were achieved (enantioselective rate ratio $k_L/k_D = 1.63$) under an O_2 atmosphere at 25°C with tetra(*p*-carboxyphenyl)porphyrin manganese(III) chloride covalently bound to *bovine serum albumin* [418].



The mechanism of oxidation of 2,6-dimethylnaphthalene in the O_2 + Mn porphyrinate/sodium borohydride system was investigated. A dioxo manganese porphyrin complex was suggested as the active oxygenating species [419]. The catalytic activity of Mn, Fe, Co, Ni, and Cu acetylacetonates in the homogeneous phase oxidation of *o*-, *m*-, and *p*-xylene was studied. Bromoacetylacetonates showed the highest activity [420]. The hydroxylation of aromatic compounds (benzene, toluene, *p*-xylene, anisole, acetanilide, nitrobenzene, and acetophenone) by O_2 in acetic acid at 90°C in the presence of metallic iron was reported [421].

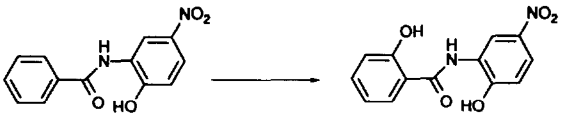
Mathematical models for plant simulation and optimization of a *p*-xylene oxidation reactor were established in order to regulate the synergistic effect of Co acetate- Mn acetate catalyst and solvents [422].

3-Methylindole was oxygenated at 25°C and 1 bar O_2 in the presence of cobalt(II) phthalocyanine attached to polyorganosiloxane as the catalyst. In homogeneous *o*-dichlorobenzene solution at 89% conversion of 3-methylindole, 24% 2-formyl-aminoacetophenone was obtained:



The rate of O_2 absorption was found to be first order in 3-methylindole, catalyst and O_2 [423]. The transformation of the $Co(OAc)_2$ catalyst precursor to active complexes with monobasic aromatic products and to inactive complexes with dibasic aromatic acids during the oxidation of *p*-xylene and methyl *p*-toluate was studied [424]. Poly(4-methylstyrene) was oxidized with O_2 in the presence of Co acetate bromide catalyst. Depending on reaction time and temperature $\leq$ 65% of the methyl groups were converted into aldehyde and carboxylic acid groups, with only moderate backbone cleavage [425].

Orthohydroxylation of **160** by the metallic copper + O_2 (1 bar) + triethylamine N-oxide system at 75°C gave **161** in 90% isolated yield [426].



160 **161**

The copper carboxylates-catalyzed oxidative di- and polymerization of phenols under O_2 was studied [427]. See also [364].

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

4.2.1. Oxidation of alcohols

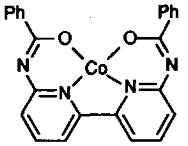
Heteropoly acids $H_{3+n}PV_nMo_{12-n}O_{40}$ were found to be moderately active catalysts for the oxidation of ethylene glycol in the temperature range 200–300°C [428]. The catalytic oxidation of benzoin to benzil with pyridine-N-oxide or air using monooxomolybdenum(IV) thiolate complexes as the catalyst at room temperature was investigated [429].

The over-oxidation of cyclohexane by the Gif system was investigated in a model oxidation reaction of cyclohexanol and cyclohexanone at 20°C and 80°C under an atmosphere of pure O_2 in order to determine their rates of oxidation and to identify the over-oxidation products formed [430]. Aerobic carbon–carbon bond cleavage of aliphatic and aryl-substituted diols catalyzed by (TPP)FeCl was investigated in the presence of an NAD(P)H model compound as a reducing agent. Based on kinetic results a mechanism involving formation of hydroxy radical or its equivalent by intramolecular one-electron transfer of diolato-iron(IV) was proposed [431].

Aerobic oxidation of benzyl alcohol, geraniol, cinnamyl alcohol, and 2-naphthylmethanol at 20°C in the presence of $RuCl(OAc)(PPh_3)_3$ + hydroquinone + $Co(salophen)(PPh_3)$ (H_2salophen = N,N′-bis(salicylidene)-*o*-phenylenediamine) catalyst system gave the corresponding aldehydes with > 98% selectivity [432]. Bis(pyridine)cobalt(II) perchlorate activates dioxygen *via* the reversible formation of a μ-dioxygen complex which oxidizes N-methylanilines, benzyl alcohol, and aldehydes with subsequent autoxidation [433]. Selective oxidation of primary allylic alcohols to α,β-unsaturated aldehydes using O_2 and fine metal particle catalysts generated from $Rh_6(CO)_{16}$ and $Rh_4(CO)_{12}$ was reported [434].

4.2.2. Oxidation of phenols

The new cobalt(II) complex (**162**) shows excellent catalytic activity for the selec-tive oxidation of 2,6-di-t-butylphenol to 2,6-di-t-butylquinone with O_2 in the presence of a base. The durability of **162** is much higher than that of Co(salen) (**163**) [435].



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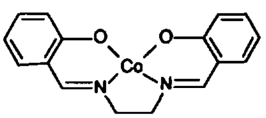
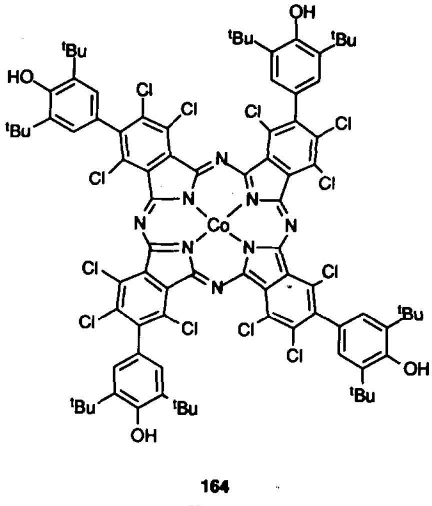


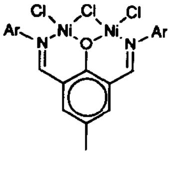
163

The oxidation of 2,6-di-t-butylphenol in the presence of cobalt Schiff base superoxo and μ-peroxo complexes gave mainly 2,6-di-t-butylbenzoquinone and 3,3′,5,5′-tetra-t-butyldiphenoquinone, respectively [436]. A cobalt complex of a polymeric ligand prepared from the polysaccharide chitosan and salicylaldehyde was used in aqueous solution to catalyze the oxidation of catechol to *o*-quinone by dissolved oxygen as the oxidant [437]. The kinetics of *p*-hydroquinone oxidation with O_2 to *p*-benzoquinone catalyzed by immobilized Co^{II} 2,2′-bipyridyl complex were studied. Michaelis-Menten kinetics were found [438]. A model system consisting of cobalt(II)-tetramine complexes and 3,5-di-t-butylcatechol was examined to elucidate the reaction mechanism of catechol dioxygenase. Based on absorption, NMR, and ESR spectra the essential role of a charge-transfer Co^{II}-semiquinone radical complex in the dioxygenase reaction was established [439]. The kinetics of the oxidation of 2-aminophenol by dioxygen in the presence of tetrakis(3,5-di-t-butyl-4-hydroxyphenyl)-dodecachlorophthalocyaninatocobalt (II) (**164**) have been investigated [440].



164

Binuclear Ni^{II} (**165**) and Co^{II} (**166**) complexes were found to be active catalysts in the oxidation of 3,5-di-t-butylcatechol to 3,5-di-t-butylquinone by O_2 [441].



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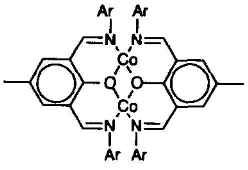
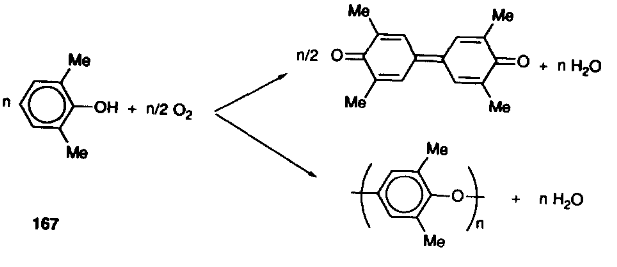


166

The oxidative coupling of **167** to polyphenyleneoxide (**168**) at 25°C and 1 bar O_2 in *o*-dichlorobenzene was selectively (99%) catalyzed by a copper-pyridine complex encapsulated in a Y-zeolite supercage. The homogeneous CuCl + pyridine + O_2 system afforded **168** with only 35% selectivity [442].



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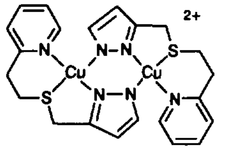
168

The kinetics and mechanism of the copper(II)-catalyzed autoxidation of catechol to *o*-quinone by molecular oxygen in aqueous solution was studied by spectroscopic methods following the reaction with a Clark oxygen electrode at 25°C [443]. The oxygenation of 3,5-di-t-butylcatechol and ascorbic acid in the presence of Cu_2LCl_3 (L = macrocyclic Schiff bases derived ligands) as the catalyst was studied [444]. The kinetics of the autoxidation of 3,5-di-t-butylcatechol catalyzed by pyrazolate-bridged dicopper(II) complexes **169** and **170** were studied by the initial rates method in 1:1 = MeOH:H_2O. The reaction is first order in the binuclear copper catalyst and O_2 and independent of the substrate. Complex **170** was found to catalyze the reaction two order of magnitude faster than **169** [445].



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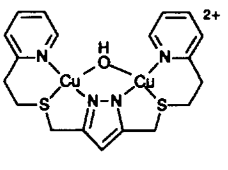


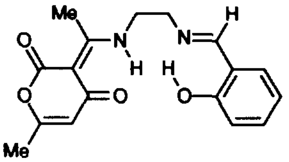
170

Dehydrogenation of 3,5-di-t-butylcatechol and t-butylhydroquinone by $FeCl_3$, $CuCl_2$, $MnCl_2$, and $CoCl_2$ with O_2 in THF was found to be greatly promoted by using the catalysts supported on SiO_2 and Al_2O_3 [446]. See also [386].

4.2.3. Oxidation of aldehydes and ketones

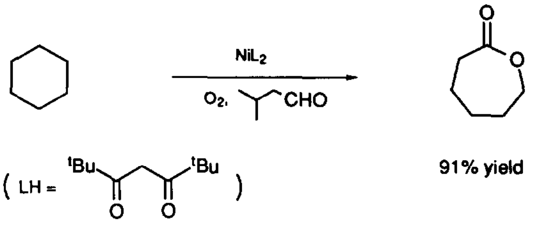
The catalytic oxidation of acetaldehyde over alkali metal salts of 12-molybdophosphoric acids was studied in relation to the redox and acidic properties of the heteropoly compounds. High oxidizing abilities and low Bronsted acidity were found to result high yields of acetic acid [447].

Some new experimental results on the oscillatory aerial oxidation of acetaldehyde, propionaldehyde, and benzaldehyde in 90% acetic acid containing cobalt(II) acetate and sodium bromide were reported. A semi-batch reactor was used to study the reaction under controlled conditions of temperature, oxygen flow-rate and reactant concentrations [448]. The Co^{II} complex of the unsymmetrical Schiff base ligand **171** was found to be an efficient catalyst for the air-oxidation of *p*-anisaldehyde to *p*-anisic acid. In cooxidation of a *p*-anisaldehyde-styrene mixture, styrene was selectively converted to styrene oxide as the major product [449].

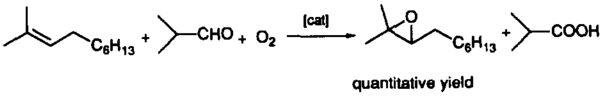


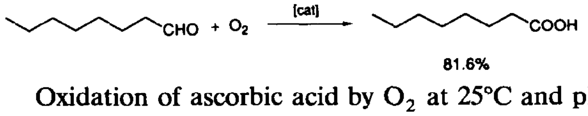
171

Various cyclic ketones were converted into the corresponding lactones or esters by O_2 (1 bar) at room temperature in the presence of an aldehyde and of a catalytic amount of nickel(II) 1,3-diketonato complexes [450]. *E.g.*:



Trisubstituted or *exo*-terminal olefins were smoothly monooxygenated at room temperature into the corresponding epoxides in high to quantitative yields by combined use of atmospheric pressure of oxygen and an aldehyde as a reductant in the presence of bis[1,3-di(*p*-methoxyphenyl)-1,3-propanedionato]nickel(II) or other bis-1,3-dionatonickel(II) complexes as the catalyst [451]. In the presence of these catalysts various aldehydes were smoothly oxidized into the corresponding carboxylic acids in good yields [452]. *E.g.*:





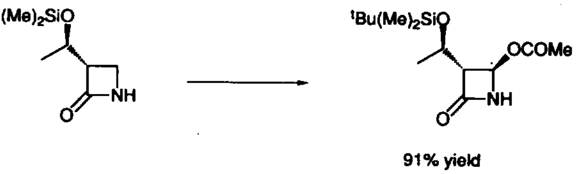
Oxidation of ascorbic acid by O_2 at 25°C and pH = 4.45 was studied polarographically. Cupric ions increased the rate of oxidation; the Cu^{II} chelate compound ethylenediaminetetraacetatocuprate had no catalytic effect [453]. See also [433].

4.2.4. Miscellaneous oxidations

Oxidation of cyclohexyl peroxide with O_2 is catalyzed by $VO(DMSO)_5(ClO_4)_2$. Spectroscopic investigations suggest the formation of an oxygen complex [454] and of several other unstable and paramagnetic species [455].

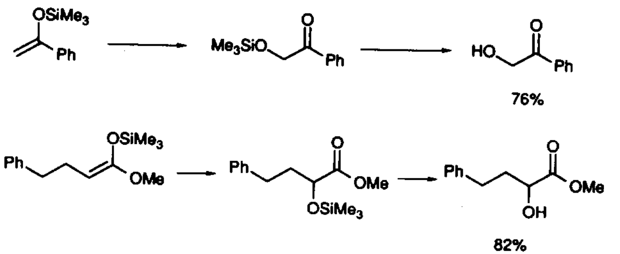
The deactivation in the Mo heteropolyacid-catalyzed oxidative dehydrogenation of isobutyric acid to methacrylic acid was studied [456].

Acetoxylation of β-lactams at C-4 position was achieved by the $RuCl_3$-catalyzed oxidation in the presence of acetaldehyde and acetic acid with molecular oxygen in ethyl acetate at 40°C [457]. *E.g.*:



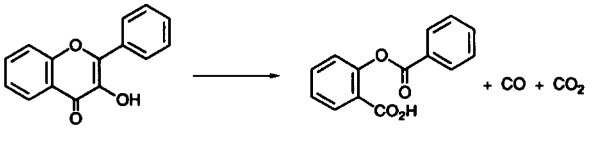
The effect of deuterated solvent on catalytic oxidation of *p*-xylene and the conjugated decarboxylation of acetic acid in the presence of $Co(OAc)_2 + NaBr$ was studied. Based on the observations, the intermediacy of a carboxylate radical in the decarboxylation was excluded [458].

N,N′-dibutylurea was obtained in up to 55% yield in the dioxygen-induced oxidative carbonylation of butylamine catalyzed by $NiBr_2(NH_2Bu)_4$ at 70°C [459]. In the presence of a catalytic amount of $Ni(mac)_2$ (mac = 3-methyl-2,4-pentanedionato), silyl enol ethers and silyl ketene acetals were smoothly oxygenated by the combined use of molecular oxygen (1 bar) and isobutyraldehyde in 1,2-dichloroethane or ethyl acetate at 25°C to afford α-siloxy carbonyl compound or after desilylation α-hydroxy carbonyl compounds [460]. *E.g.*:



Catalytic hydroxylation of unactivated C–H bonds of aliphatic acids with moderate to high regioselectivity was achieved using a $K_2PtCl_4 + K_2PtCl_6 + O_2$ system in water at 80–90°C. The following order of reactivity was found: $\alpha\text{-C–H} \ll \beta\text{-C–H} < \gamma\text{-C–H} \geqq \delta\text{-C–H} \approx \epsilon\text{-C–H}$ [461].

Catalytic oxygenation of **172** in the presence of Cu^I and Cu^{II} flavonolate complexes gave **173**, CO and CO_2 as the primary products at 80°C with up to 98% conversions [462,463].



172 **173**

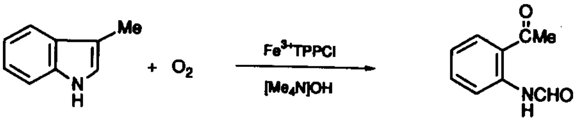
Copper(II) in aqueous NH_4OH in conjunction with O_2 or $K_2S_2O_8$ as an auxiliary oxidant has been applied to induce oxidative cleavage of ketones to nitriles [464].

$$PhCOCOOH \longrightarrow \underset{51\%}{PhCN} + PhCOOH$$

$$Me_2C(OH)COMe \longrightarrow \underset{70\%}{MeCN} + MeCOMe$$

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

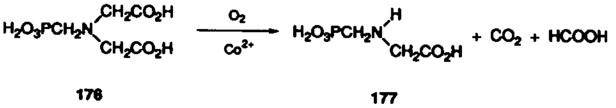
N-Propyl-1,4-dihydronicotinamid was oxidized by O_2 in the presence of $[Fe(CN)_6]^{3-}$ in aqueous EtOH or MeCN solutions. The reaction is first order in both substrate and ferricyanide [465]. The mechanism of dioxygenation of **174** to **175** in the presence of Fe^{III}TPPCl was studied by means of spectroscopic measurements and product analysis [466].



174 **175**

The kinetics of oxidation of Et_2NH and Et_3N with molecular oxygen catalyzed by $Ru^{II}(EDTA\text{-}H)(H_2O)$ were studied between 25 and 45°C at pH 2.0 [467]. The kinetics of the oxidative carbonylation of methylamine catalyzed by dichloro(salicylaldehyde-*o*-phenylenediiminatoruthenate(III) at 150°C and 21 bar $CO:O_2 = 1:0.5$ to give mainly (80%) methylurethane were studied [468].

The cobalt(II) ion-catalyzed oxidative dealkylation of one carboxymethyl group in **176** by molecular oxygen (55 bar) at 85°C in aqueous solution gave selectively **177** [469]. The same reaction was studied also in the presence of vanadyl sulfate as the catalyst [470].



176 **177**

The kinetics of the O_2-oxidation of 2-aminofenol to 2-aminophenoxazine-3-one catalyzed by tetrakis(3,5-di-t-butyl-4-hydroxyphenyl)dodecachlorophthalocyanatocobalt(II) were studied by spectrophotometry. The reaction is first order in catalyst and obeys a Michaelis-Menten type kinetics with respect to 2-aminophenol. A mechanism was suggested which involves rate-determining metal ion mediated electron transfer from coordinated 2-aminophenol to coordinated O_2 in the superoxo complex [471].

The catalytic oxidative deamination of (*p*-sulfophenyl)glycine by molecular oxygen with Cu^{2+} and pyridoxal derivatives as the catalyst was reported [472].

4.4. Catalytic oxidation of Si-, P-, or S-containing organic compounds with O_2

Oxidation of $HSCH_2CH_2OH$ with O_2 was studied using polycarboxy-phthalocyanato complexes of Co, Fe, Ni, and Cu. The metal and the number of carboxylato groups affected the catalytic activity; catalytic activities decreased in the following order (the number of COOH groups in parentheses): Co^{II},(8) > Fe^{III},(8) > Co^{II},(4) > Fe^{II},(4) [473].

$RuBr_2(Me_2SO)_3$ as a catalyst gave 90% yield of $O{=}PPh_3$ in O_2 oxidation of PPh_3 in refluxing n-butanol [474].

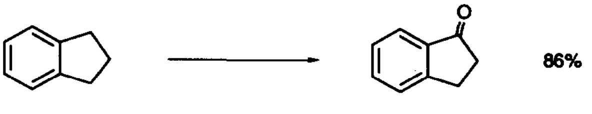
The oxidation of mercaptans in the presence of Co-phthalocyanine adsorbed on a mineral oxide support was investigated. The 50-fold greater rate of oxidation of n-dodecyl mercaptan than that of t-butyl mercaptan under the same conditions was attributed to steric hindrance [475]. Co^{II}-tetraphenoxyphthalocyanine on charcoal showed an increased activity in mercaptan oxidation in the presence of additives such as *p*-chloranil, phenazine, and NH_3 [476]. Low molecular weight, polymeric, and covalently bound cobalt(II)-phthalocyanines were found to be efficient catalysts for the oxidation of 2-mercaptoethanol [477]. Cationic latex particles prepared by emulsion copolymerization of styrene and divinylbenzene were used as a support for tetra-Na phthalocyaninatocobalt(II)tetrasulfonate. This latex-bound system increased the reaction rate of oxidative coupling of 2-mercaptoethanol as compared with the polymer-free system using the same complex as catalyst. The stability of the polymer-anchored catalyst was, however, rather poor [478]. On silica immobilized phthalocyanines cobalt(II) 2,9,16,23-tetracarboxyphthalocyanine was found to exhibit high catalytic activity in the oxidation of 2-mercaptoethanol with O_2 to the corresponding disulfide at 25°C and 1 bar pressure [479].

$RhCl(PPh_3)_3$ was found to catalyze the aerobic oxidation of hexyldimethylsilane to hexyldimethylsilanol at 40°C [480].

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

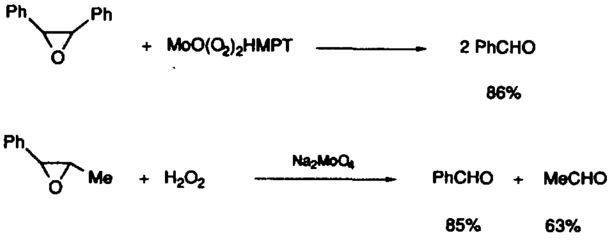
4.5.1. Oxidation of hydrocarbons or hydrocarbon groups

The relative reactivities of several substituted toluenes towards oxometalloporphyrin complexes, O=M(TPP)Cl (M = Fe, Cr, Mn) generated by the reaction of the corresponding M^{III}(TPP)Cl with iodosobenzene was investigated. Selectivities towards hydrogen atom abstraction decreased in the order Cr=O > Fe=O > Mn=O in accord with the force constants of the M=O bonds [481]. A good yield of α-indanone (**178**) was obtained in the chromium(VI)-catalyzed benzylic oxidation of indane with t-butylhydroperoxide [482].

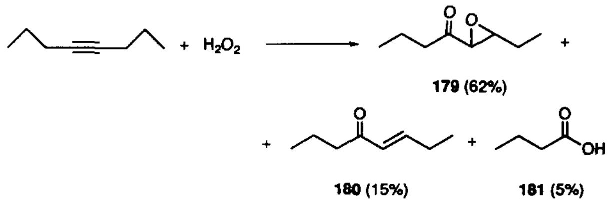


178

The oxidative cleavage of the oxirane ring to carbonyl compounds at 40°C by molybdenum(VI) peroxo complexes in a stoichiometric reaction or in a two-phase catalytic system with H_2O_2 was studied [483]. *E.g.*:

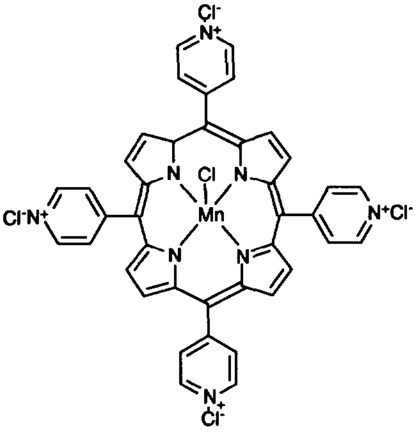


Trimethoxybenzenes were oxidized to dimethoxy-*p*-benzoquinones in 50–60% yield with H_2O_2 in the presence of Mo and W heteropolyacids in acetic acid or formic acid [484]. In the presence of peroxotungstophosphates under two-phase conditions 4-octyne gave the corresponding α,β-epoxy ketone (**179**), α,β-unsaturated ketone (**180**), and a small amount of cleaved product **181** [485].



Thermal and photochemical alkane functionalization reactions (oxidation with ᵗBuOOH and photodehydrogenation) catalyzed by oxidatively resistant metalloporphyrin analogs and isopolytungstates were studied [486].

Oxidation of 1,3-dimethyluracil with cumene hydroperoxide using (TPP)MnCl or (Cl$_8$TPP)MnCl as catalysts in the presence of imidazole or N-methylimidazole gave 5-hydroxy-1,3-dimethyluracil and 6-hydroxy-1,3-dimethyluracil [487]. Manganese and iron complexes of the bis-pocket porphyrin (5,10,15,20-tetrakis(2′,4′,6′-triphenyl-phenyl)porphyrin) were found to catalyze the hydroxylation of alkanes and the epoxidation of nonconjugated dienes with a wide variety of oxidants [488]. High yields and rates were found for hydroxylation of alkanes in presence of **182** intercalated with HSbP$_2$O$_8$, FeOCl or montmorillonite [489].



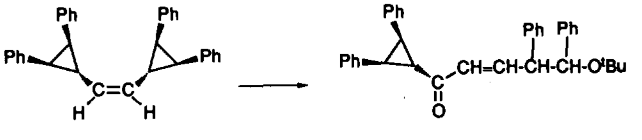
182

Olefin epoxidation and aliphatic and aromatic hydroxylations by PhIO in the presence of Mn^{III}, Fe^{III}, or Co^{II} substituted polyoxotungstate complexes was investigated and compared to results with metalloporphyrin catalysts [490]. The hydroxylation of phenol to pyrocatechol and hydroquinone by H$_2$O$_2$ in the presence of metal phthalocyanines as the catalysts was investigated [491].

The oxidation of progesterone by the GoAgg^{III} system (aqueous H$_2$O$_2$, FeCl$_3$, picolinic acid in pyridine + acetic acid solution) was studied. Two triketo derivatives and an unstable formyl derivative were isolated and identified as the products [492]. Fe^{III} complexes, [Fe(TPA)X$_2$](ClO$_4$) (TPA = tris(2-pyridylmethyl)amine; X = Cl, Br, N$_3$) were found to be excellent reagents for the oxidative functionalization of alkenes using ^{t}BuOOH. Thus, from cyclohexane cyclohexyl-X was formed selectively in 70–80% yield [493]. Iron(II) picolinate and iron(II) 2,6-dicarboxylato-pyridine catalyze the selective ketonization of methylenic carbons in cyclohexane, n-hexane, ethyl benzene and cyclohexene with hydrogen peroxide, and the dioxygenation of arylolefins to aldehydes in pyridine/acetic acid solvent at 22°C [494]. Binor S (**183**) was regiospecifically oxidized to **184** by H$_2$O$_2$ in pyridine catalyzed by ferric picolinate complexes [495].

183 **184**

The intermediate species in the tetrakis(4-N-methylpyridyl)porphyrinato-iron(III)-catalyzed oxidation of cyclohexene to cyclohexanol by PhIO was studied by UV-Vis and ESR spectroscopic techniques at low temperature. Iron(III)porphyrin rhombic species, oxo iron(IV)porphyrin, and iron(III) N-oxide species were detected [496]. Polymeric polyhalogenated iron(III) porphyrin catalysts for hydrogenation of cyclohexane and for epoxidation of norbornene with pentafluoroiodosylbenzene were studied [497]. Oxidation of *cis*-stilbene and **185** by ^{t}BuOOH at room temperature in the presence of (TMP)Fe^{III}(Cl), (Cl$_8$TPP)Fe^{III}(Cl), (Br$_8$-TPP)Fe^{III}(Cl) resulted as main product *trans*-stilbene oxide and **186**, respectively [498].



185 **186**

Iron porphyrins containing perhalogenated pyrroles were found to be much better catalysts for the hydroxylation of pentane or heptane by PhIO at 20°C in CH$_2$Cl$_2$ than the corresponding iron porphyrins without halogens on the pyrrole rings. Yields as high as 80% were obtained [499].

The kinetics of phenol hydroxylation by H$_2$O$_2$ in the presence of ferric sulfate was studied [500]. Hydroxylation of phenol and O-protected phenols in the Fe^{III} + catechol + H$_2$O$_2$ system showed enhanced *para*-selectivity in the presence of β-cyclodextrin [501].

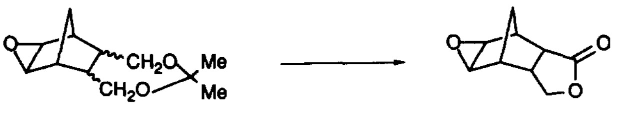
Supporting evidence of a free-radical mechanism for the hydrocarbon activation in a cyclodecane + FeCl$_3$ + H$_2$O$_2$ + pyridine + acetic acid system leading to cyclodecanone was reported [502]. Simple iron complexes, such as [Fe$_2$OCl$_6$](NEt$_4$)$_2$, [Fe$_2$O(phen)$_4$(H$_2$O)$_2$](ClO$_4$)$_4$ and [{Fe(ala)$_2$(H$_2$O)}$_3$O](ClO$_4$)$_7$ were found to be good catalysts for oxidation of cyclohexane to cyclohexanol and cyclohexanone by ^{t}BuOOH at 25°C (phen = phenanthroline; ala = alanine). Addition of imidazole improved the efficiency and the selectivity of the reaction [503].

It was found that sulfide formation can replace oxidation in Gif-type (iron-carbon) chemistry. Dicyclohexyl di- and poly-sulfides were formed when cyclohexane was subjected to Gif-type oxidation conditions in the presence of sufficient H$_2$S, Na$_2$S or S$_8$. Similar sulfuration of cyclooctane and of norbornane has been observed under Gif^{III} conditions [504]. The oxidation of cyclohexane by ${}^tBuOOH$ or H_2O_2 to cyclohexanol and cyclohexanone was catalyzed by $Fe_2(TPA)_2(O)(ClO_4)_4$ at 25°C (TPA = tris(2-pyridylmethyl)amine) [505].

The oxidation of levulinic acid to succinic and formic acids by N-bromoacetamide in the presence of mercuric acetate as scavenger and ruthenium(III) chloride as catalyst was studied. The mechanistic implication of kinetic data was discussed [506]. The molecular characterization of Messel kerogen was carried out by selective oxidation-degradation with $RuO_4 + NaIO_4$ at 25–35°C. The kerogen was almost completely (> 95%) oxidized. Mainly n-monocarboxylic acids and C_{4-30}-α,ω-dicarboxylic acids were formed [507]. The ruthenium(IV)-oxo complex $[Ru^{IV}(terpy)(dcbipy)O]^{2+}$ (terpy = 2,2′ : 6′,2″-terpyridine; dcbipy = 6,6′-dichloro-2,2′-bipyridine) was found to be a powerful oxidant which can selectively oxidize the tertiary C–H bond of adamantane. The complex $[Ru^{II}(terpy)(dcbipy)(H_2O)]^{2+}$ showed catalytic activity for the oxidation of saturated alkanes by ${}^tBuOOH$ [508]. The complex, *cis*-$[Ru(dpm)_2(Solv)_2](PF_6)_2$ (dpm = 2,9-dimethyl-1,10-phenanthroline, Solv = MeCN or H_2O) was found to hydroxylate methane at 4 bar and 75°C using H_2O_2 or hypochlorite as the primary oxidant in water or acetonitrile. 125-140 turnovers per day were reported [509]. The catalytic oxidation of alkenes, alkanes, and thioethers with H_2O_2 in the presence of $Ru(dpm)^{2+}$ was studied [510].

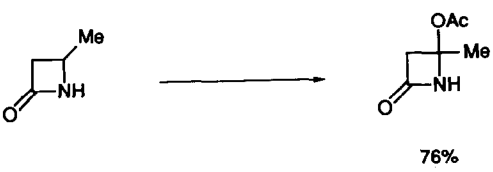
The RuO_4-catalyzed $NaIO_4$ oxidation of **187** and **189** gave **188** and **190**, respectively [511].

187 **188**

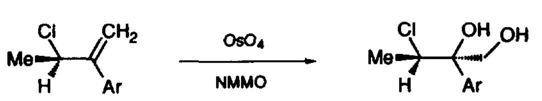


189 **190**

Room temperature activation of aliphatic C–H bonds in cyclohexane and pentane was observed in the reaction of $Os_3(CO)_{11}(NCMe)$ and $Te(CF_3)_2$ leading to $Os_3(CO)_{11}Te(C_6H_{11})_2$ (90% yield) and to $Os_3(CO)_{11}Te(C_5H_{11})_2$ (78% yield). The first alkane was functionalized thermally at room temperature. The activation of the second alkane required sunlight [512]. The OsO_3-catalyzed oxidation of β-lactams with peracetic acid gave the corresponding 4-acetoxy β-lactams in good to excellent yields. *m*-Chloroperbenzoic acid, methyl ethyl ketone peroxide, $PhI(OAc)_2$ and PhIO as oxidant gave lower yields than peracetic acid [513]. *E.g.*:



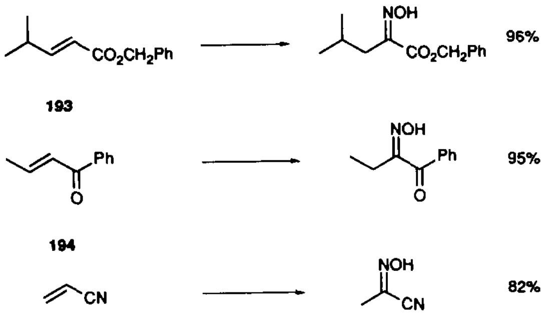
Treatment of **191** with a catalytic amount of osmium(VIII) oxide and excess N-methylmorpholine N-oxide in THF-water was found to give the (2*R*,3*R*) diol **192** with ca 10 : 1 diastereoselectivity in 72% isolated yield [514].



191 **192**

The oxidation of cyclohexane by cumene hydroperoxide in the presence of benzene solutions of cobaltous complexes of tetra-4-t-butylphthalocyanine and tetra-t-butyltetrazaporphine at 20°C was studied. In the case of the former complex the reaction was catalyzed not only by the complex itself but by the product of its reversible oxidation on the macrocycle [515]. The influence of peripheral substituents and axial ligands in cobaltous phthalocyanine derivatives on velocity and mechanism of cyclohexane oxidation with cumene hydroperoxide was studied. The interesting phenomenon of catalyst stabilization by cyclohexyl radicals due to their axial coordination was detected [516].

Various α,β-unsaturated compounds, such as **193**, **194**, **195**, and **196** were directly converted to the corresponding α-hydroximino compounds in high yields on treatment with butyl nitrite and phenylsilane in the presence of a catalytic amount of **197** at room temperature [517].



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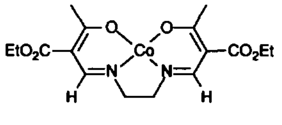
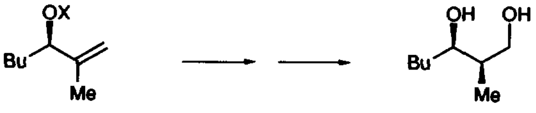


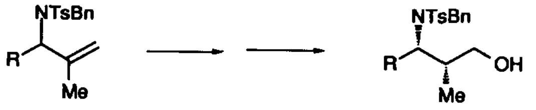
197

Methane was selectively oxidized with a mixture of 30% H_2O_2 and trifluoroacetic anhydride to methyl trifluoroacetate in a Pd^{II}-catalyzed reaction at 90°C and 62 bar CH_4-pressure. In the presence of 7.5 mol% Pd^{II} propionate 38% yield (based on H_2O_2) was achieved in 24 h [518].

Predominantly *syn* products were obtained in the rhodium-catalyzed hydroboration and subsequent H_2O_2 oxidation of allylic alcohol derivatives **198** [519] and allyl amine derivatives **199** [520] using $[Rh(COD)Cl]_2$ and catecholborane.

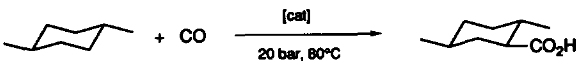


198 X = H, Ac, $COCF_3$, CO^tBu, CPh_3

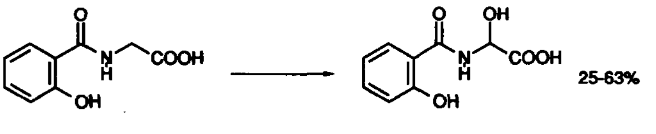


199 R = $PhCH_2$, Bu, $^iPrCH_2$;

The oxidation of benzene to phenol with hydrogen peroxide catalyzed by α-pyrrolidonate-bridged mixed-valent tetranuclear platinum complexes, with the general formula of $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{n+}$ ($n = 4, 5, 6, 8$), has been examined [521]. Carboxylation of alkanes with CO *via* direct thermal activation of the alkane C–H bond by a $Pd(OAc)_2 + K_2S_2O_8 + CF_3COOH$ catalyst system to give carboxylic acids was reported [522]. *E.g.*:

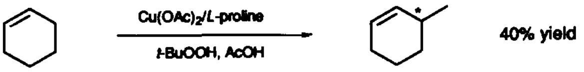


In the case of cyclohexane the low (1.95) turnover number of the catalytic reaction was increased up to 200 by addition of $Cu(OAc)_2$ [523]. The Cu^{II}-catalyzed oxidation of adamantane by H_2O_2 in pyridine + acetic acid solution gave mainly 2-adamantanone as the reaction product with *ca.* 20–30% conversion [524]. The oxidation of cyclohexene with $H_2S_2O_8 + CuSO_4$, 52% cyclopentanecarboxylic acid and 23% 1,2-cyclohexanediol cyclic sulfate were formed [525]. The oxidation of cyclohexene to mainly allylic oxidation products and styrene to styrene oxide by t-butyl hydroperoxide was catalyzed by copper(II) complexes of tris(2-benzimid-azolylmethyl)amine at 60°C [526]. The oxidation of cyclododecane by aqueous H_2O_2 catalyzed by Cu^{II}, Fe^{III}, Co^{II}, Ru^{III}, and Ni^{II} salts in pyridine-MeCN mixtures gave *ca.* 25% alkane conversion mainly to cyclododecanone and 10% efficiency for H_2O_2 [527]. α-Hydroxylation of **200** with the copper-containing oxidation systems: $Cu + O_2 +$ pyridine, $Cu^{II} + H_2O_2 +$ pyridine, and $Cu^{II} + Me_3NO + MeCN$ gave **201** in moderate yield [528].

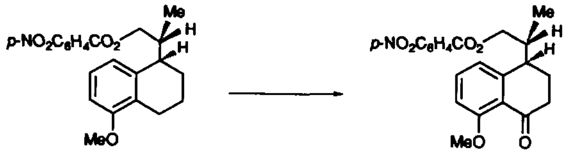


200 **201**

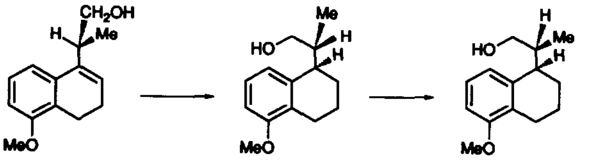
Cyclohexene, AcOH, ^tBuOOH, and catalytic amounts of both copper acetate and L-amino acids gave (*S*)-acetylcyclohexene at 70°C with up to 30% ee [529]:



The oxidation of **202** with $K_2S_2O_8 + CuSO_4 +$ *sym*-collidine and with pyridine chlorochromate gave **203** in 63% yield. The precursor of compound **202** was prepared from **204** at 4 bar H_2 in THF at 23°C in the presence of $RhCl(PPh_3)_3 + {}^tBuOK$ as the catalyst, affording **205** and **206** in > 95 : 5 ratio [530].

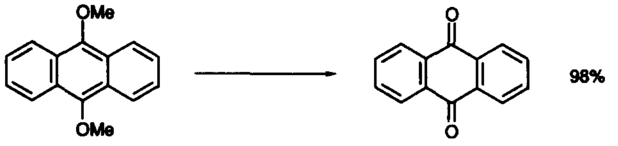


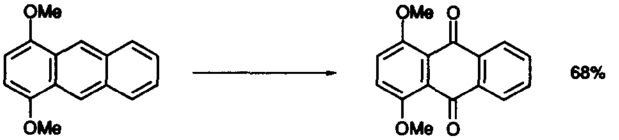
202 **203**



204 **205** **206**

The reactions involved in the copper ion-catalyzed oxidation of cyclohexene by persulfate to yield cyclopentanecarbaldehyde were elucidated from the kinetics of the reaction of the intermediate 2-hydroxycyclohexyl free radicals with $Cu^{2+}(aq)$ [531]. Anthraquinones were obtained by selective oxidation of the corresponding anthracenes and 9,10-dimethoxyanthracenes with copper or zinc nitrate supported on silica gel in boiling CCl_4 [532]. *E.g.*:

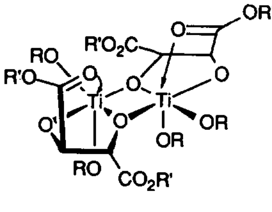




See also [370].

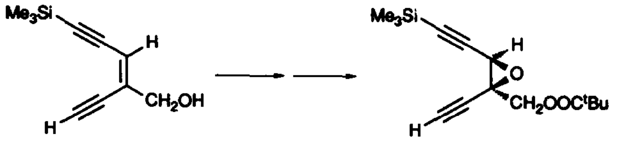
4.5.2. *Epoxidation of olefins*

The kinetics and the catalyst structure of the Sharpless asymmetric epoxidation reaction for allylic alcohol substrates were studied. The rate law under pseudo-first-order conditions in CH_2Cl_2 for several different substrates and tartrate esters over a wide concentration range in Ti-complex was found to be: rate = k[allylic alcohol][Ti-tartrate][ROOH][inhibitor alcohol]$^{-2}$. From the reaction rates obtained with various Ti-tartrate stoichiometry, it was concluded that an equimolar complex of titanium tetraalkoxide and tartrate diester is the catalytically active template for asymmetric epoxidation [533]. One major species, a dimeric 2:2 Ti-tartrate complex **207**, was identified as the active catalyst based on the results of molecular weight measurements, MS, IR, ^1H, ^{13}C and ^{17}O NMR spectroscopy [534].



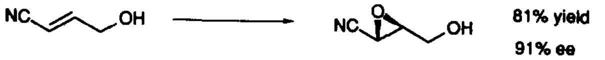
207

The catalytic version of the Sharpless asymmetric epoxidation (5 mol% $Ti(O^iPr)_4$; (−)-diethyl tartrate, ^tBuOOH, CH_2Cl_2, −5°C, 36 h) and *in situ* esterification of the product with pivaloyl chloride was applied to obtain the (*R*,*R*)-epoxy diyne **209** in 83% yield and 93% ee from the corresponding (*Z*)-endiyne **208** [535].



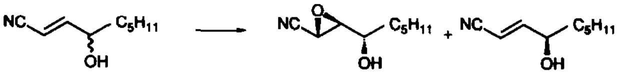
208 **209**

The Sharpless asymmetric epoxidation of **210** afforded a potentially useful chiral building block **211**.



210 **211**

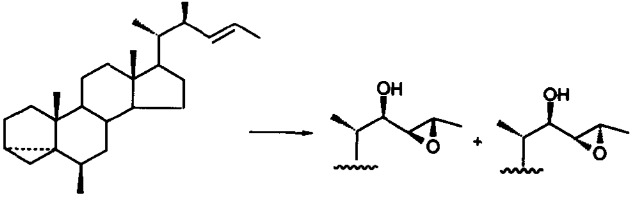
Under the same conditions kinetic resolution of racemic-**212** resulted in **213** and (*R*)-**212** [536].



212 **213** (*R*)-**212**

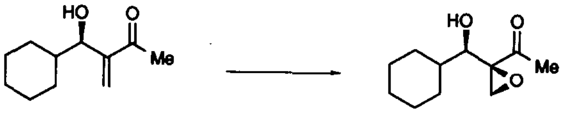
40% yield, 95% ee

The catalytic Sharpless epoxidation (using L-(+)-diethyl tartrate and molecular sieves) of **214** afforded the diastereomers **215** and **216** in 70:30 proportion with 95% yield. The epoxidation of **214** with ^tBuOOH in the presence of $VO(acac)_2$ in toluene gave a 5:95 ratio of **215** and **216** in 90% yield [537].



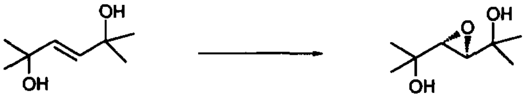
214 **215** **216**

Epoxidation of **217** using $Ti(O^iPr)_4$ or $VO(acac)_2$ catalysts gave **218** in 78% (99% stereoselectivity) and 76% (> 99% stereoselectivity) yield, respectively [538].



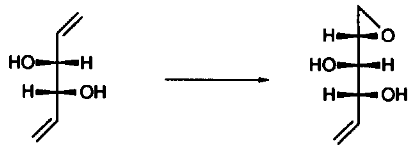
217 **218**

The asymmetric Katsuki–Sharpless epoxidation (L-(+)-diisopropyl tartrate, $Ti(O^iPr)_4$, ^tBuOOH, 4A molecular sieve, −20°C) of **219** gave 96% yield and 70% ee of **220** [539].

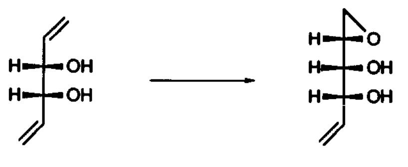


219 **220**

The Katsuki–Sharpless asymmetric epoxidation was applied to obtain the epoxides **223** and **224** from **221** and **222**, respectively [540].

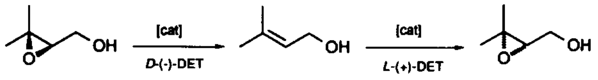


221 **223**



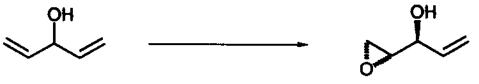
222 **224**

The Sharpless epoxidation of **225** using various organic hydroperoxides was investigated. The best results, 45–50% yield and 90% ee, were obtained with ${}^tBuOOH$ [541].



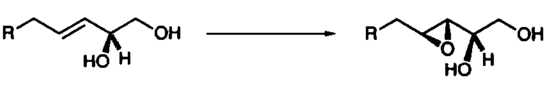
225

The Sharpless epoxidation was applied to prepare **227** from **226** [542].



226 **227**

The Katsuki–Sharpless asymmetric epoxidation of **228** was found to proceed only in the presence of diisopropyl L-(+)-tartrate leading to exclusive formation of **229** [543].



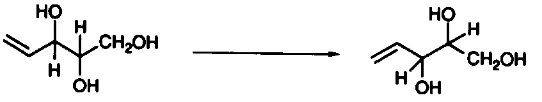
228 **229**

R = OCH_2Ph, $N(Tos)CH_2Ph$, Bu, Ph,$H_2C{=}CH(CH_2)_3$, $Me(CH_2)_{13}$

The Sharpless asymmetric epoxidation ($Ti(O^iPr)_4$, ${}^tBuOOH$, (−)-diethyl tartrate, −30°C) of **230** gave **231** with 98% yield [544].

230 **231**

The symmetric stereoselective Sharpless epoxidation was used to obtain **232** and **233** from divinyl carbinol after hydrolysis of the resulting 1,2-epoxy-4-pentene-3-ols [545,546].

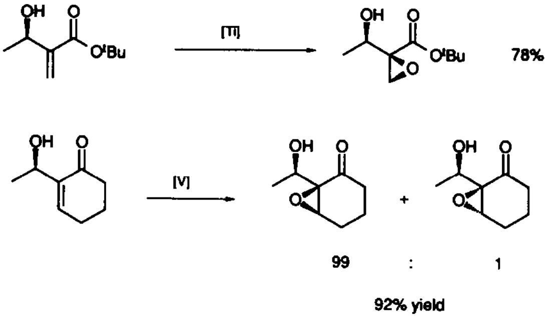


232 **233**

The asymmetric epoxidation of geraniol using chiral titanium complex with amino alcohol derived ligand gave up to 83% ee of **234** [547].

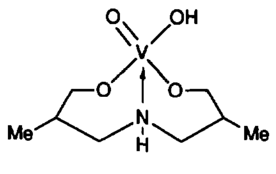
234

The epoxidation of β-hydroxyacrylates and cyclic β-hydroxyketones using $Ti(O^iPr)_4 + {}^tBuOOH$ or $VO(acac)_2 + {}^tBuOOH$ in CH_2Cl_2 at −15°C gave selectively the *syn* product [548]. *E.g.*:



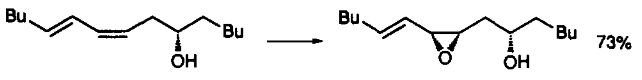
In the presence of vanadyl acetylacetonate, iodosobenzene is a useful oxidant for the epoxidation of Δ^5-steroids into epoxides. Most of the steroids tested gave mainly the β-epoxides, oxidation of cholest-5-ene-3-one occurred, however, with high α-selectivity [549]. In the presence of t-butyl hydroperoxide and a catalytic amount of $VO(acac)_2$, steroidal γ-hydroxy-α,β-unsaturated ketones possessing an allylic hydroperoxy group were found to behave in the same manner as simple allylic alcohols in cyclic systems without conformational flexibility. Equatorial OH groups gave mainly oxidation products (2-ene-1,4-diones), in most instances accompanied by *cis*- and *trans*-2,3-epoxy-4-hydroxy-1-ones in a ratio of ~ 3:1. Axial OH groups gave *cis*-2,3-epoxy-4-hydroxy-1-ones accompanied by small amounts of the corresponding 2-ene-1,4-diones [550].

Vanadatranes, $VO(OCH_2CH_2)_3N$ and $VO[OCH(CH_3)CH_2]_3N$, and complex **235** were found to catalyze the epoxidation of propene and cyclohexene with t-butyl hydroperoxide. In the presence of **235**, propylene oxide was formed with 80% selectivity [551].



235

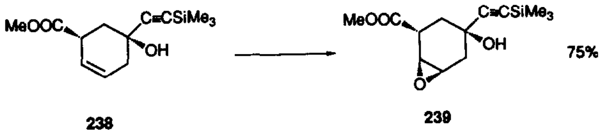
The stereoselective homoallylic hydroxyl group directed epoxidation of **236** to **237** with VO(acac)$_2$ and t-butyl hydroperoxide in CH$_2$Cl$_2$ has been applied [552].



236 **237**

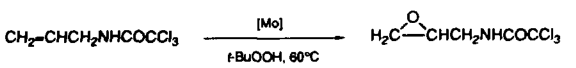
[Cr(bpb)(H$_2$O)$_2$]ClO$_4$, [Cr(bpb)Cl(MeOH)], and [Mn(bpc)(OAc)] (H$_2$bpb = 1,2-bis(pyridine-2-carboxamido)-benzene; H$_2$bpc = 4,5-dichloro-1,2-bis(pyridine-2-carboxamido)benzene) was found to catalyze olefin epoxidation by PhIO. With [Mn(bpc)(OAc)] catalytic oxidation of alkanes by PhIO was observed. An O-rebound mechanism involving a Mn^V(=O) or a Cr^V(=O) intermediate was proposed for the PhIO oxidation reaction [553].

Epoxidation of **238** by t-butyl hydroperoxide in refluxing benzene in the presence of Mo(CO)$_6$ gave the epoxide **239** in 75% yield [554].



238 **239**

Allyl chloride was epoxidized with t-butyl hydroperoxide and different molybdenum catalysts; of the 18 Mo compounds tested, the best results were obtained with MoCl$_5$, Mo(CO)$_6$, and Mo(acac)$_3$ [555]. The complex CpoO$_2$Cl was found to act as a catalyst of the reaction of alkyl hydroperoxides and olefins to yield the corresponding epoxides and alcohols [556]. In the presence of Mo(O)$_2$(acac)$_2$, **240** was oxidized by t-butyl hydroperoxide to give **241**. Optical inductions up to 45% were achieved by using diisopropyl tartarate as ligand [557].

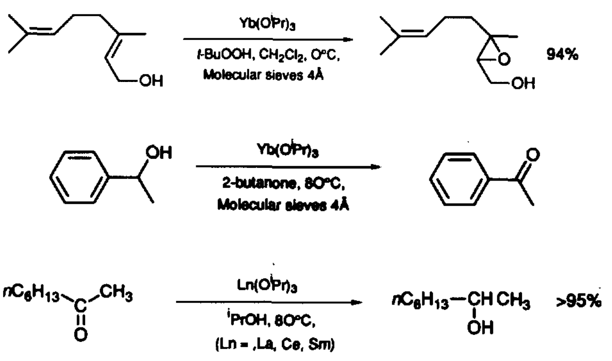


$$CH_2{=}CHCH_2NHCOCCl_3 \xrightarrow[t\text{-BuOOH, 60°C}]{[Mo]} H_2C\overset{O}{—}CHCH_2NHCOCCl_3$$

240 **241**

Epoxidation of cyclohexene with H$_2$O$_2$ was investigated in the presence of Mo^{VI} and W^{VI} catalysts in a biphasic water–chlorobenzene system. Tungsten(VI) was found to be about three times as active as Mo^{VI}. Arsenate and phosphate ions promoted the reaction [558]. The dependence of the epoxide yield on the concentrations of H$^+$, metal ion (Mo, W), phase-transfer catalyst, and promoter ion was studied [559]. The role of molybdenum(VI) peroxides in biphasic epoxidation with H$_2$O$_2$ was investigated [560]. The catalytic epoxidation of *cis-,trans-,trans*-1,5,9-cyclododecatriene with t-butyl and cumyl hydroperoxides in the presence of molybdenum compounds was studied. MoO$_5$-(HMPA)$_2$O was found to be the most active catalyst [561].

Lanthanide (La, Ce, Sm, and Yb) alkoxides have been found to catalyze the epoxidation of geraniol with t-butyl hydroperoxyde and the Meerwein–Ponndorf–Verley–Oppenauer reactions [562]. *E.g.*:

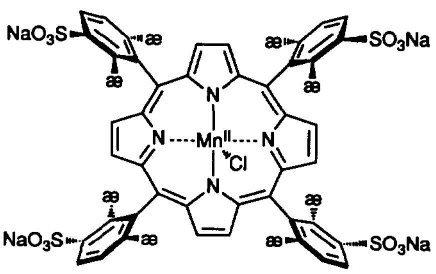


The epoxidation of styrene with t-butyl hydroperoxide in the presence of immobilized molybdenum complexes on inorganic and polymeric matrices was studied [563]. Epoxidation of cyclohexene with aqueous H$_2$O$_2$ catalyzed by ammonium molybdate bound to 60 nm colloidal anion exchange polymers gave 90% conversion to > 99% cyclohexene oxide at 40°C [564]. Cyclooctene epoxidation catalysts were prepared from a quaternized (with Et$_3$N or Bu$_3$P) (chloromethyl)-styrene–divinylbenzene polymer by anion exchange with peroxomolybdate derived from ammonium molybdate or phosphomolybdic acid in 80% aqueous H$_2$O$_2$ [565]. The activation, activity, and stability of polymer-supported molybdenum and vanadium catalysts was studied in cyclohexene epoxidation with t-butyl hydroperoxide [566].

The epoxidation of 1-octene with H$_2$O$_2$ in a biphase medium was studied using tungsten and molybdenum-based catalyst precursors. Based on UV, IR, Raman, ^{31}P and ^{183}W NMR spectroscopy it appears that $\{PO_4[Mo(O)(O_2)_2]_4\}^{3-}$ is responsible for the catalytic activity of phase transfer systems involving H$_3$[PM$_{12}$-O$_{40}$] as a precursor [567]. Epoxidation of unsaturated acids with H$_2$O$_2$ in the presence of phosphotungstic acid was found to be first order in substrate and zero order in H$_2$O$_2$. A mechanism was suggested [568]. An *in situ* formed catalyst from Na_2WO_4, H_3PO_4 or NaH_2PO_4 and 10% aqueous H_2O_2 containing $PhCH_2$-N(n-octyl)$_3^+Cl^-$ in 1,2-dichloroethane was used to convert $RCH{=}CH_2$ ($R =$ n-hexyl, n-pentyl, Ph, $ClCH_2$, $BrCH_2$) and 2-octene to the corresponding epoxides with $\leq 96\%$ selectivity [569]. A novel triperoxyniobium-containing polyoxoanion $SiW_9(NbO_2)_3O_{37}^{7-}$ was found to catalyze the epoxidation of allyl alcohols with aqueous H_2O_2 in MeCN solution at reflux temperature [570].

Manganese β-octachloro-*meso*-tetrakis(2,6-dichlorophenyl)porphyrin was used as catalyst in oxidation of alkenes and alkanes with H_2O_2 at room temperature. The highest reported yield was 99% in the case of cyclooctene oxide formation [571]. The effects of various oxidatively-stable ligands and bases were studied in epoxidation of alkenes with H_2O_2 catalyzed by manganese-porphyrins. The advantageous use of adducts of H_2O_2 was described [572]. The epoxidation of styrene by NaOCl in the presence of manganese tetraphenylporphyrin as the catalyst was investigated. The effect of the axial ligand, the solvent, and the phase transfer catalyst was studied [573]. Propene was epoxidized by Mn(TPP)Cl catalyst with NaOCl in the presence of an axial ligand, phase transfer agent, and solvent. 4-Benzylpyridine as axial ligand led to higher catalytic activity than 4-methylpyridine. 80% yield and 100% selectivity was reported [574]. The role of the axial ligand in *meso*-tetraphenyl manganese- and ironporphyrin models of the P-450 cytochromes in cyclohexene oxidation with iodosobenzene as an oxygen source was studied. It was proposed that s-donation can accelerate oxene transfer from the catalyst to the substrate, while π charge donation can additionally alter the energy of the acceptor orbital on the active catalyst that is responsible for initiating substrate oxidation. With $[Mn(TPP)(H_2O)_2]ClO_4$ in benzonitrile 80% yield of cyclohexene oxide was obtained [575].

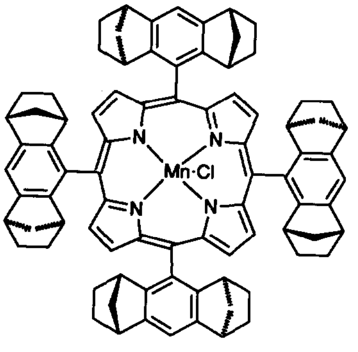
A detailed mechanistic study of epoxidation of alkenes with sodium hypochlorite/manganese(III) tetraarylporphyrin was published [576]. Quaternized (chloromethyl)styrene-divinylbenzene copolymer treated with Mn-5,10,15,20-tetrakis(2,6-dichloro-3-sulfonylphenyl)porphyrin was found to catalyze the epoxidation of styrene with NaOCl to give styrene oxide [577]. The epoxidation of styrene with aqueous NaOCl catalyzed by **242** bound to colloidal anion-exchange particles was found to be more active than the free catalyst in aqueous solution: 0.12 mol% of **242** bound to different types of particles gave 71–81% conversion of 1.2 mmol styrene to styrene oxide with 1.5 mmol NaOCl in 1h at room temperature. Aliphatic alkenes such as 1-decene, cyclooctene, and *cis*-stilbene did not react under those conditions [578].



242

The reaction of olefins with ozone in the presence of catalytic amounts of the manganese or iron complex of β-octabrominated tetramesitylporphyrin afforded modest yields of epoxides besides the main products of the noncatalyzed direct ozonolysis [579].

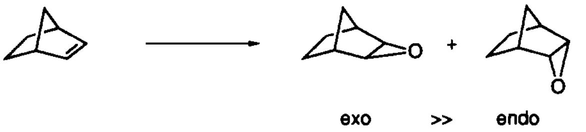
The asymmetric epoxidation of *para*-chlorostyrene with iodosobenzene in the presence of iron and manganese glycoconjugated porphyrins was studied [580]. Catalytic asymmetric epoxidation of aromatic-substituted alkenes with NaOCl under phase-transfer conditions using **243** as catalyst afforded yields above 90% and enantioselectivities ranging from 41 to 76% ee [581].



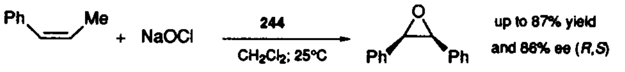
243

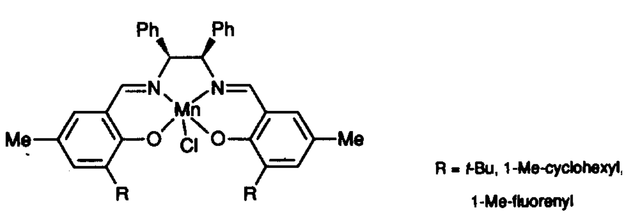
The catalytic epoxidation of cyclooctene with 30% H_2O_2 at 0°C in the presence of a Mn^{III}-tetraarylporphyrin bearing an imidazole axial ligand and a carboxylic group juxtaposed on opposite sides of the porphyrin plane was studied [582].

The epoxidation of olefins (1-octene, cyclohexene, cyclooctene, 1-methylcyclo-hexene and norbornene) with iodosobenzene using Fe or Mn complexes of 2,4,6,8-tetratrifluoromethyl-1,3,5,7-tetraethylporphyrin as the catalyst was investigated. Comparisons with the octaethyl-porphyrin + iodosobenzene systems have shown that the electronic effect in porphyrin ring does not affect the *exo/endo* selectivity of norbornene oxidation [583].



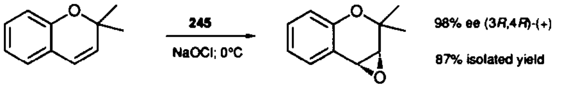
A practical method for the asymmetric epoxidation of *cis*-β-methylstyrene with commercial bleach as the stoichiometric oxidant and a chiral salen-based Mn^{II} epoxidation catalyst **244** was described [584].

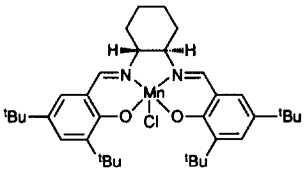




244

A highly effective process for the asymmetric epoxidation of several 2,2-dimethylchromene derivatives with NaOCl using **245** as the catalyst was reported [585]. *E.g.*:





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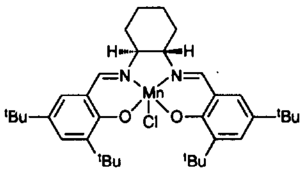
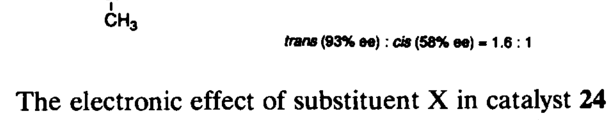
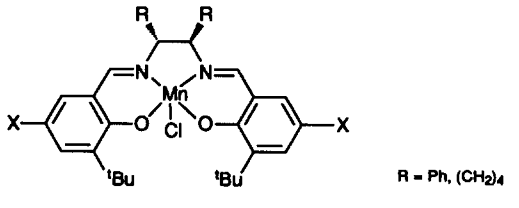


246

Enantioselective epoxidation of conjugated dienes and enynes with NaOCl catalyzed by **246** at room temperature was reported [586]. *E.g.*:

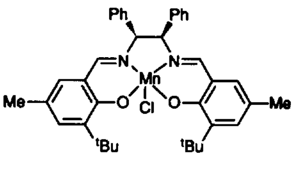


The electronic effect of substituent X in catalyst **247** on the enantioselectivity of epoxidation of different prochiral olefins with NaOCl was investigated. In all cases the same trend was observed, with electron-donating groups on the catalyst leading to higher enantioselectivities in epoxidation [587].



247

Highly enantioselective epoxidation of *cis*-β-methylstyrene with NaOCl catalyzed by **248** (up to 86% ee) [588] and **249** (up to 98% ee [589] was reported.



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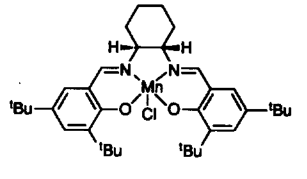
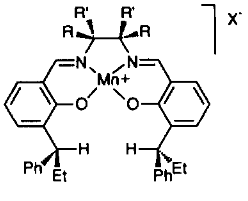


249

Chiral manganese(III) complexes, **250** and **251** were used for catalytic asymmetric epoxidation of unfunctionalized olefins with PhIO as a terminal oxidant. Donor ligands such as pyridine N-oxide or 2-methylimidazole was found to alter the enantioselectivity. The highest enantioselectivity was achieved for (*E*)-1-phenylpropene (56% ee, with **250** (R = H, R′ = Ph, X = PF_6)) in the presence of 2-imidazole, (*E*)-stilbene (48% ee, with **251** (R = Ph, R′ = H)), and dihydronaphthalene (83% ee, with **251** (R = Ph, R′ = H) in the presence of pyrimidine N-oxide [590]. In the case of (*Z*)-1-phenylpropene 68–72% ee was achieved [591].



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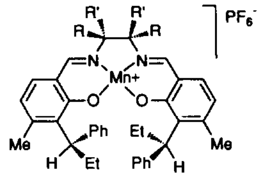


251

The epoxidation of alkenes with HOCl or 30% H_2O_2 in the presence of different Mn^{III}-tetraarylporphyrins as the catalyst was investigated [592]. Iron and manganese porphyrin complexes with an oxygen or nitrogen ligand in proximal position were found to catalyze the epoxidation of cyclohexene with H_2O_2 [593]. The epoxidation of olefins by H_2O_2 using Mn^{III} porphyrin and benzoic acid in a two-phase catalytic system was studied. An increase in the rate of epoxidation was observed in the presence of polydentate esters [594]. The enantioselective epoxidation of styrene with NaOCl and the H_2O_2 oxidation of *p*-$R'C_6H_4SCH_2CO_2R$ (R = Me, Bu, Ph; R′ = H, Me) using manganese(III)-tetraphenylporphyrin + *bovine serum albu-*

min system modified or unmodified with poly(ethylene glycol) was reported [595].

Methyltrioxorhenium was found to be a highly active and selective catalyst for the H_2O_2 oxidation of a carbon–carbon double bond to an epoxide. In the absence of a nitrogen base more or less 1,2-diol was the product [596]. *E.g.*:

$$\beta\text{-Pinene} + H_2O_2 \xrightarrow[t\text{-BuOH, 5°C}]{MeReO_3} \underset{40\%}{\beta\text{-pinene oxide}} + \underset{50\%}{\beta\text{-pinane-1,2-diol}}$$

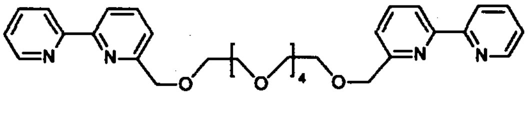
The ferric complex, $(Et_3HN)Fe^{III}(bpb)X_2$ (H_2bpb = 1,2-bis(2-pyridinecarbox-amido)benzene, X = Cl, OTf) was found to catalyze the epoxidation of a variety of olefins (cyclohexene, stilbene, styrene, norbornene, 1-octene) by iodosylbenzene [597]. Novel chiral biaryl-modified iron-porphyrin complexes were used in catalytic and asymmetric epoxidation of styrene derivatives with iodosobenzene. The best chiral induction (89% ee) was recorded for 2-nitrostyrene [598].

The epoxidation of cyclohexene and (*Z*)-cyclooctene with iodosylbenzene using ionic iron(III) tetraarylporphyrins as catalysts supported on cross-linked polystyrene ion-exchange resins was studied in methanolic solutions. The epoxidation is favored by increased crosslinking of the resin support [599]. The epoxidation of (*Z*)-cyclooctene by iodosylbenzene catalyzed by cationic iron(III) tetra(N-methylpyridyl)-porphyrins adsorbed onto the highly crosslinked cation ion-exchange resin Dowex MSC1 gave up to 59% yield of epoxide along with *ca.* 30% formaldehyde [600].

Competitive epoxidation of norbornylene and α-methylstyrene by *m*-chloroper-oxybenzoic acid in the presence of a catalytic amount of iron (III) porphyrins in CH_2Cl_2 and toluene at −78°C and room temperature was reported [601].

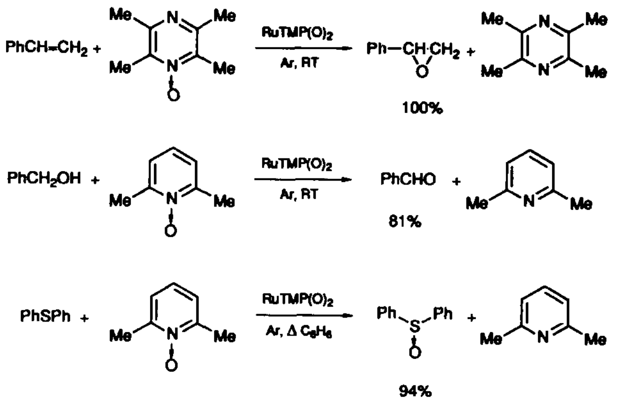
Iron complexes of cyclam (1,4,8,11-tetraazacyclotetradecane) and related ligands were found to be highly efficient catalysts for olefin epoxidation by aqueous 30% hydrogen peroxide [602].

The kinetics of the epoxidation of *cis*-cyclooctene, styrene, and *trans*-stilbene with H_2O_2 catalyzed by Ru^{III} + EDTA + ascorbate system was studied [603]. *trans*-Stilbene was epoxidized with $NaIO_4$ or KIO_4 to *trans*-stilbene oxide in the presence of ruthenium(II) complexed with 2,2′-bipyridine or **252** as the catalyst in a biphasic system [604].

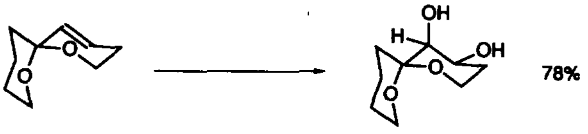


252

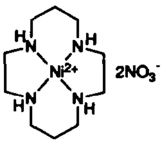
Olefins, alcohols, and sulfides were converted into epoxides, aldehydes, and sulfoxides, respectively, with various heteroaromatic N-oxides in the presence of catalytic amounts of [dioxo(tetramesitylporphyrinato)-ruthenium(VI)], ($RuTMP(O)_2$) [605]. *E.g.*:



Highly stereoselective *syn*-hydroxylation of unsaturated spiroketals using a catalytic amount of OsO_4 and N-methylmorpholine-N-oxide in aqueous acetone at room temperature was reported [606]. *E.g.*:



Cobalt-Schiff base complexes were found to catalyze the oxidation of olefins with NaOCl at 25°C to give mainly epoxides together with *vic*-dichloro- and α-chloro-carbonyl compounds. A mechanism was proposed [607]. The epoxidation of styrene, cyclohexene, and some other olefins with NaOCl at room temperature in the presence of nickel complexes of bidentate heterocyclic amines as catalyst was studied [608]. Certain square planar Ni^{II} complexes such as **253**, **254**, and **255** were found to be active catalysts for hydrocarbon oxidation reaction (epoxidation, hydroxylation, and C=C bond cleavage) with hypochlorite (**254** and **255**) or with PhIO (**253**) [609].



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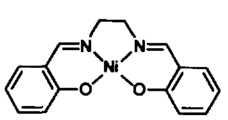

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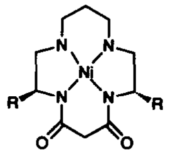


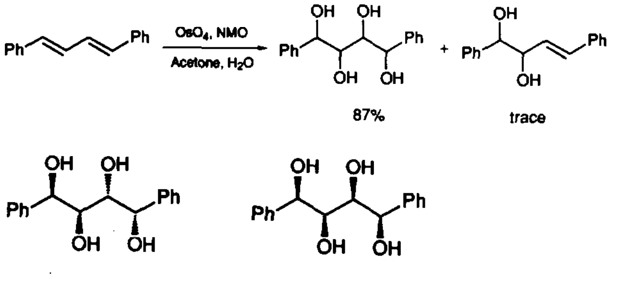
255

See also [488,490,497,498,526].

4.5.3. Dihydroxylation of olefins

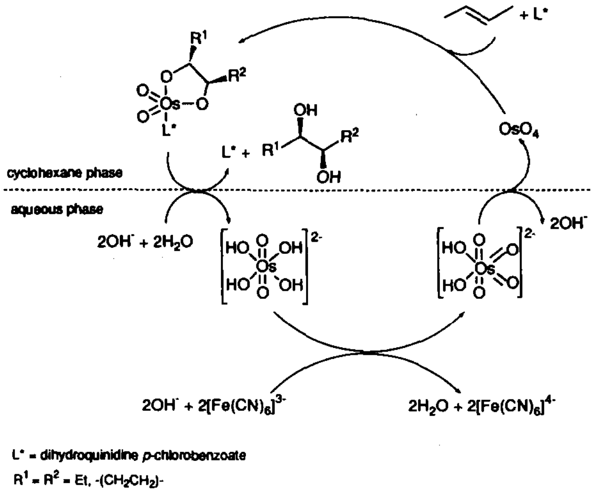
Alkenes, like octadecene, octadec-9-ene, and cyclohexene were hydroxylated to vicinal diols in 60–80% yield by aqueous H_2O_2 in 1,4-dioxane as solvent using 1 mol% Re_2O_7 as catalyst [610].

The dihydroxylation of cis-3,4-disubstituted cyclobutenes with OsO_4 took place with moderate to high *syn* selectivity in the case of Cl, OAc, and OSO_2M substituents [611]. A one-pot stereoselective synthesis of polyols by catalytic osmylation of conjugated dienes in the presence of stoichiometric amount of N-methylmorpholine N-oxide (NMO) has been reported [612]. *E.g.*:



16 : 1

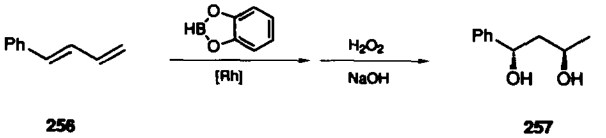
Asymmetric dihydroxylation of olefins with N-methylmorpholine N-oxide was achieved using OsO_4 and 9-*O*-acylquinine-acrylonitrile copolymer ligand as catalyst [613]. The OsO_4-catalyzed asymmetric dihydroxylation of olefins using potassium ferricyanide as the reoxidant was studied. Based on preparative and spectroscopic evidences a catalytic reaction sequence was proposed [614] as shown below:



L* = dihydroquinidine *p*-chlorobenzoate
$R^1 = R^2 = Et, -(CH_2CH_2)-$

Up to 93% enantiomeric excesses of the diols were obtained in the osmium-catalyzed asymmetric dihydroxylation of terminal olefins using ethers of dihydroquinidine and dihydroquinine as ligands [615]. The highest enantioselectivities for various olefins were obtained in the osmium-catalyzed asymmetric dihydroxylation using 9-*O*-aromatic dihydroquinidine and dihydroquinine ligands. A ligand structure-enantioselectivity relationship was developed [616].

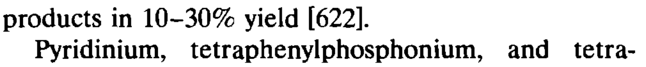
The rhodium (*R*)-BINAP-catalyzed asymmetric double hydroboration of **256** afforded after oxidation **257** in up to 67% ee [617].



256 **257**

4.5.4. Oxidation of O-containing functional groups

4-t-Butylperoxy-2,5-cyclohexadien-1-ones were obtained in good yields by the oxidation of 2,4,6-trialkylsubstituted phenols with t-butylhydroperoxide in the presence of heteropolyacids such as $H_3PMo_{12}O_{40} \cdot nH_2O$ at 30°C [618]. The use of methyltrioctylammonium tetrakis(oxodiperoxotungsto)phosphate(3−) in combination with H_2O_2 as the primary oxidant in a biphase system proved to be a versatile catalytic method for alcohol and aldehyde oxidation [619]. A novel oxidation of *vic*-diols with 35% H_2O_2 into α-hydroxy ketones using peroxotungstophosphate as catalyst in a biphasic system was reported [620]. *E.g.*:



The kinetics of oxidation of α-ketoglutaric acid by bromate with ferroin as catalyst in sulfuric acid solutions were determined. An α-ketoglutaric acid-ferriin complex was proposed as intermediate [621].

In Gif-oxidation of limonene, α-terpineol, terpineol acetate, and 3-carene, ketones were obtained as major products in 10–30% yield [622].

Pyridinium, tetraphenylphosphonium, and tetraphenylarsonium salts of the anionic halodioxoruthenate(VI) complexes $[RuO_2X_4]^{2-}$, $[RuO_2Br_3]^-$, and $[RuO_2Cl_3(OPPh_3)]^-$ (X = Cl, Br) catalyze the oxidation of primary alcohols to aldehydes and of secondary alcohols to ketones with N-methylmorpholine-N-oxide as oxidant. Olefinic bonds are not affected [623].

The kinetics of the Ru^{III}-catalyzed oxidation of the hydroxy acids: lactic, tartaric, malic, and citric acid by N-bromosuccinimide in aqueous $HClO_4$ and in the presence of $Hg(OAc)_2$ were studied [624]. The kinetics of the RuO_4-catalyzed oxidation of cyclopentanol and cyclohexanol to the corresponding ketones were studied using alkaline $KBrO_3$ as the oxidant and $Hg(OAc)_2$ as the bromide ion scavenger [625]. The kinetics of the ruthenium(III)-catalyzed oxidation of erythritol (1,2,3, 4-tetrahydroxy-butane) and dulcitol (1,2,3,4,5,6-hexahydroxyhexane) by N-bromoacetamide in $HClO_4$ to erythrionic acid and galactonic acid, respectively, were studied [626]. The RuO_4-catalyzed oxidation of cyclopentanol and cyclohexanol by alkaline hexa-cyanoferrate(III) to the final products pimelic acid and acetic acid, respectively, was studied [627].

The dioxo complexes $[Ph_4P][RuO_2(OOCR)Cl_2]$ and $[Ph_4P][OsO_2(OOCR')Cl_2]$ ($R = Me$, Et, ^nPr, CF_2H; $R' = Me$, Et) were used as catalysts for oxidations of alcohols to aldehydes or ketones in the presence of N-methylmorpholine-N-oxide as co-oxidant at room temperature. Yields up to 99% were reported [628].

Selective oxidation of secondary alcohols to ketones and of primary alcohols to aldehydes were achieved by using hypochlorite in the presence of catalytic amounts of ruthenium(II) complexes in a biphasic water + dichloromethane system. Up to 30 turnovers per minute were observed at 22°C [629]. Primary alcohols such as 1-hexanol, benzylalcohol, and hydroxycitronellol were oxidized by NaOCl to aldehydes in the presence of $RuCl_3$ and $RuO_2 \cdot nH_2O$ as the catalyst. Conversions were usually higher than 75% with selectivities between 70 and 90% [630].

It was discovered that $[(C_4Ph_4COHOCC_4Ph_4)(\mu\text{-}H)][(CO)_4Ru_2]$ in the presence of a catalytic amount of formic acid catalyzes efficiently the homogeneous bimolecular disproportionation of aliphatic and aromatic aldehydes to give esters:

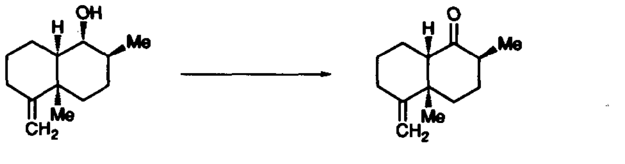
$$2\,RCHO \xrightarrow[65\text{-}100^\circ C]{[Ru]} RCOOCH_2R$$

High conversion, excellent yield and selectivity and overall turnover number of *ca.* 20000 was observed [631].

The kinetics of ruthenium(III)-catalyzed oxidation of aliphatic esters by bromamine-T in aqueous perchloric acid medium were studied. Zero order in [oxidant] and $[H^+]$ and fractional order in [ester] and $[Ru^{III}]$ was found. The activation parameters were reported [632]. The kinetics of the Os^{VIII}-catalyzed oxidation of glycols by alkaline $[Fe(CN)_6]^{3-}$ is zero order in oxidant, first order in catalyst and less than first order in glycol. The rate dependence on $[OH]^-$ is a combination of two rate constants; one independent of and the other first order in $[OH]^-$. This suggests two parallel pathways with two different Os^{VIII}-glycol complexes as intermediates [633].

The complex $OsCl_2(PPh_3)_2$(1,2-benzosemiquinone) was found to be efficient as a catalyst for the oxidation of primary alcohols to aldehydes and of secondary alcohols to ketones in the presence of N-methylmorpholine-N-oxide as cooxidant in CH_2Cl_2 solution at room temperature [634]. The oxidation of alcohols with N-methyl-morpholine-N-oxide in the presence of $OsCl_2(PPh_3)_2(acac)$ was studied and compared with that of the related Ru^{III} complexes [635].

Oxidation of **258** with N-methylmorpholine N-oxide in the presence of tetrapropylammonium perruthenate and 4Å molecular sieves afforded **259** in 96% yield [636].



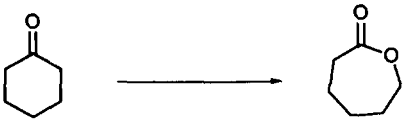
258 **259**

The kinetics of the OsO_4-catalyzed oxidation of deoxybenzoin and *p*-nitro-deoxybenzoin by alkaline hexacyanoferrate(III) were studied in 30 vol% $^tBuOH + H_2O$ mixture at a constant ionic strength. The reaction is first order each in substrate, OsO_4, and OH^-, but zero order in $Fe(CN)_6^{3-}$ [637]. The kinetics of Os^{VIII}-catalyzed oxidation of *myo*-inositol by alkaline hexacyanoferrate(III) was studied [638].

The influence of temperature, partial pressure, and cobalt(III) acetylacetonate loading on cyclohexanol conversion and product distribution in liquid-phase catalytic ozonation of cyclohexanol to cyclohexanone and adipic acid was studied [639].

Oxidation of C_1–C_3 alcohols and benzyl alcohol by periodate in the presence of Rh^{III} was found to be zero order in IO_4^-, fractional order in alcohol, and first order in Rh^{III}. The rate decreased with an increase in $[OH^-]$. The disproportionation of a complex formed between alcohol and Rh^{III} was suggested as the rate-determining step [640]. Octanal or octanoic acid was obtained in high yields from 1-octanol and sodium bromate using $RuCl_3 \cdot 3H_2O$ as catalyst precursor in a two-phase system [641]. The kinetics of oxidation of citric acid and tartaric acid by N-bromoacetamide in the presence of $HClO_4$ and $IrCl_3$ have been studied [642]. The kinetics of the iridium(III) chloride-catalyzed oxidation of methanol, ethanol, propanol-1, and butanol-1 by alkaline hexacyanoferrate(III) were investigated. The reaction follows direct proportionality with respect to the $IrCl_3$ concentration and is first order in hexacyanoferrate(III) at low concentrations. At higher concentrations the reaction becomes independent with respect to hexacyanoferrate(III) and hydroxide ions [643].

The molecular pathway of the catalytic oxidation of secondary alcohols to ketones with hydrogen peroxide using $[(dppe)Pt(CF_3)(CH_2Cl_2)]ClO_4$ as catalyst was studied. The homolytic nature of the reaction was tested with radical scavengers and radical initiators [644]. Baeyer-Villiger oxidation of cyclic ketones at room temperature with 32% H_2O_2 using [(dppe)Pt-$(CF_3)(CH_2Cl_2)$]BF_4 as catalyst has been reported [645]. *E.g.*:



The kinetics and mechanism of Cu^{II}-catalyzed oxidation of mandelic acid by peroxydisulfate ion was studied [646]. See also [429,484,605].

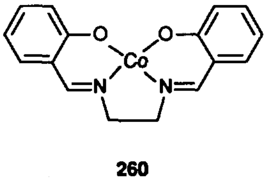
4.5.5. Oxidation of N-containing organic compounds

The *cis*-dioxoperoxo complexes, $Mo(O)_2(O_2)(RNH_2)_2$ (R = benzyl or cyclohexyl) were found to to act as catalysts in the oxidation respectively of benzyl amine to benzaldehyde oxime and cyclohexyl amine to cyclohexanone oxime with H_2O_2 at room temperature [647].

The kinetics of ruthenium(III)-catalyzed oxidation of RNH_2 (R = Me, Et, Pr, Bu), Me_2NH and Me_3N by Ce^{IV} to give NH_3 and an aldehyde or ketone as products were investigated [648]. The kinetics of ruthenium(III)-catalyzed oxidations of glycine, alanine, valine, leucine, phenylalanine, and serine by chloramine-T in the presence of chloride ion were studied [649].

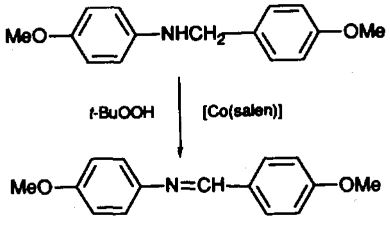
The ruthenium trichloride-catalyzed oxidation of nitrogen-heterocycles at 30°C with NaOCl was investigated. Quinoline afforded quinolic acid in up to 84% isolated yield. Isoquinoline was oxidized to cinchomeronic acid (44%) and phthalic acid (13%) [650].

The oxidation of oximes with t-butyl hydroperoxide to give the parent carbonyl compounds was catalyzed by Co(salen), **260** at room temperature [651].



260

Selective formation of imines from the corresponding secondary aromatic amines were found in cobalt Schiff base complex-catalyzed oxidations with t-butyl hydroperoxide at 40°C in DMSO solution [652,653]. *E.g.*:



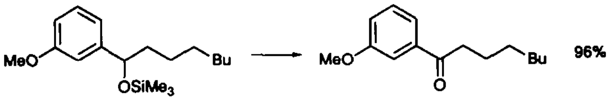
A nickel vanadyl phosphate catalyst, prepared from V_2O_5, NH_2OHCl, H_3PO_4 and $NiCl_2$ in a mixture of benzyl alcohol and isobutyl alcohol was found to catalyze the oxidation of benzylamine to benzonitrile (92% yield) with $K_2S_2O_8$ + NaOH in CH_2Cl_2 at room temperature [654].

The kinetics of the silver(I)-catalyzed oxidation of benzamide to benzoic acid and N_2 with peroxydisulfate anion were studied. The rate of peroxydisulfate disappearence is proportional to peroxydisulfate and silver(I) ion concentrations, but is independent of benzamide concentration. A free-radical mechanism involving silver(II) was proposed [655].

4.5.6. Oxidation of Si-, P-, S-, or Br-containing organic compounds

Up to 63% ee of phenyl methyl sulfoxide was obtained in the [TiCl(chiral-salen)$_2$]O-catalyzed oxidation of phenyl methyl sulfide by triphenylmethyl hydroperoxide. The rate of the reaction was found to be first order in each sulfide, hydroperoxide, and complex catalyst [656].

Secondary benzylic and allylic trimethylsilyl ethers were oxidized at room temperature to the corresponding ketones in high yield using aqueous 70% t-butyl hydroperoxide and catalytic amounts of $(Ph_3SiO)_2CrO_2$ [657]. *E.g.*:



A kinetic study of the oxidation of DMSO by Ce^{IV} catalyzed by Cr^{III} indicated that Cr^{IV}, which is formed in an equilibrium step, is the active oxidant [658]. Triphenylphosphine oxide was formed in oxygen atom transfer reaction from dimethyl sulfoxide and N_2O to triphenylphosphine mediated by the pentacyanooxomolybdate (IV) anion [659]. Aryl methyl sulfoxides were formed quantitatively from aryl methyl sulfides and hydrogen peroxide in chloroform/ethanol (4:1) solution at −20°C in the presence of cetylpyridinium tetrakis(diperoxomolybdo)phosphate as the catalyst. The kinetics of the reaction were studied [660].

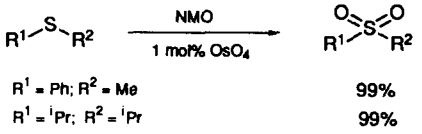
A chiral iron porphyrin, prepared by condensation of (*S*)-(+)-2-(6-methoxy-2-naphthyl)propionyl chloride with 5α,10β,15α,20β-tetrakis(*o*-aminophenyl)porphyrin, catalyzed the asymmetric oxidation of sulfides to sulfoxides in a PhIO + imidazole + CH_2Cl_2 system at 0°C. 60–84% yields and 5–15% ee were reported [661]. Chloro *meso*-tetraphenylporphyrinato iron(III) supported on silicagel was found to catalyze the selective oxidation of sulfides to sulfoxides with iodosylbenzene as oxidant [662]. *E.g.*:

$$PhSPh \xrightarrow[\text{r. t.; } CH_2Cl_2]{\text{PhIO, [cat]}} \underset{74\%}{PhS(O)Ph} + \underset{0\%}{PhS(O)_2Ph}$$

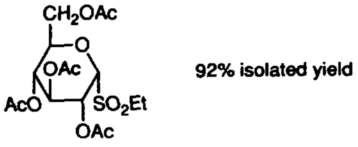
Sulfides were oxidized with N-methylmorpholine N-oxide in the presence of *cis*-$RuCl_2(DMSO)_4$ as catalyst. Based on kinetic measurements a mechanism was proposed [663].

The kinetics and mechanism of the oxidation of triphenylphosphine with $KHSO_5$ catalyzed by a propylenediaminetetraacetato complex of ruthenium(III) in water + dioxane have been studied [664]. The oxidation of triphenylphosphine to triphenyl-phosphine oxide with iodosylbenzene catalyzed by N-hydroxyethyl + ethylenediamine + triacetatoruthenate(III) was studied [665].

Osmium tetroxide was found to be an effective and general catalyst for the oxidation of sulfides to sulfones with N-methylmorpholine N-oxide at room temperature [666]. *E.g.*:



Sulfides were selectively oxidized to sulfones (such as **261**) by N-methylmorpholine N-oxide or trimethylamine N-oxide at room temperature in the presence of a catalytic amount of OsO_4 [667].

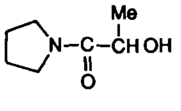


261

See also [510,595,605].

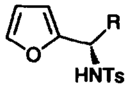
4.5.7. *Kinetic resolution by asymmetric oxidation*

A new kinetic resolution of unfunctionalized oxiranes by *in situ* formed chiral molybdenum(VI)(oxodiperoxo) hydroxy acid amide/aliphatic diol complexes has been reported. Thus at 23°C in 1,2-dichloroethane a mixture of racemic 2,3-dimethyl-oxirane : $MoO(O_2)_2$ · (*S*)-PYLA : (3*S*)-2-methyl-butane-2,3-diol = 5 : 1 : 2 gave (2R,3R)-dimethyloxirane in 48% chemical yield and 99.7% ee ((*S*)-PYLA = **262**) [668].



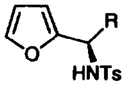
262

Kinetic resolution of α-furfuryl amide has been achieved by using the modified Sharpless reagent ($Ti(O^iPr)_4$, L-(+)- or D-(−)-DIPT, CaH_2, silica gel, and ${}^tBuOOH$) at room temperature. (*S*)-**263** and (*R*)-**263** were obtained in high enantioselectivity (90–100% ee) and high chemical yield (45–50% [669].



(*S*)-263

R = Me, Et, Pr, ⁿBu, ⁱBu, ⁿHx

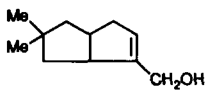


(*R*)-263

R = Et, ⁿHx

Dependence of kinetic resolution efficiency on the monodentate alkoxyde ligands of the bystander titanium center in the asymmetric epoxidation of secondary allylic alcohols was revealed and the implications of the effect were discussed [670].

Kinetic resolution by asymmetric oxidation was applied in preparation of **265** and **266** from racemic **264** [671].



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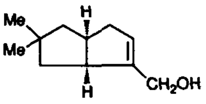

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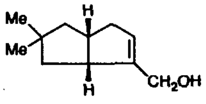
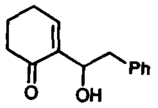
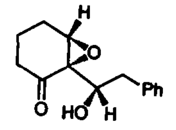


266

The kinetic resolution of racemic **267** with (+)-diisopropyl tartarate, CH_2Cl_2, $Ti(O^iPr)_4$, ${}^tBuOOH$, $FeSO_4 \cdot 7H_2O$ and citric acid monohydrate afforded 39% *syn*-epoxide **268** and 35% (*R*)-**267** [672].

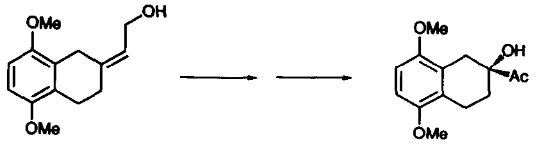


267



268

The double kinetic resolution techniques in Sharpless epoxidations were discussed with the aim of optimizing yields and enantiomeric excesses of optically active products [673]. The Sharpless asymmetric epoxidation was applied in the preparation of **270** from **269** [201].



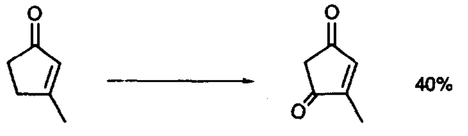
269 **270**

See also [536,541,543].

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

4.6.1. Oxidation of hydrocarbons or hydrocarbon groups

A novel allylic oxidation of conjugate ketones with $VO(OR)Cl_2$ was reported. An oxo group was introduced regioselectively at the γ-position of **271** on treatment with $VO(O^iPr)Cl_2$ in isopropanol solution under an O_2 atmosphere. Selective alkoxylation was the reaction course in the case of **272** under a N_2 atmosphere [674].



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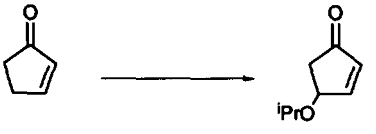
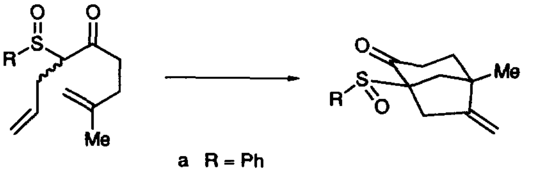


272

Allylic oxidations of ursolic acid with CrO_3 + pyridine complex at room temperature was reported [675]. An oxidizing agent prepared from CrO_3 and Me_3SiCl was used for benzylic oxidations of toluenes and alkylbenzenes. Thus, $4\text{-}MeOC_6H_4Me$ afforded 59% $4\text{-}MeOC_6H_4CHO$ and $^nPrC_6H_5$ afforded 82% $EtC(=O)C_6H_5$ [676].

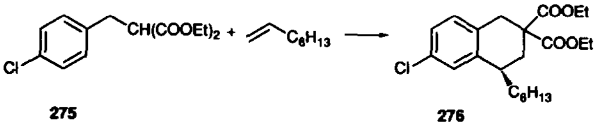
The kinetics of oxidation of toluenes and phenanthrenes by quinolinium dichromate in the presence of an acid were studied. The rate of the reaction was found to be first order in each substrate, oxidant, and acid. The rate data obey Hammett's relationship. Values of ρ for toluenes (-0.20) and phenanthrenes (-1.79) were obtained. For the oxidation of toluenes into the corresponding aldehyde, $k_H/k_D = 5.13$ was observed [677]. Rate constants for the oxidation of substituted benzenes by aqueous CrO_3 containing HCl and $K_4Ru_2OCl_{10}$ in a spray reactor at 323 and 371 K increased in the order: PhCl, $PhCF_3$, C_6H_6, $PhCMe_3$, $PhCD_3$, $PhCH_3$, $C_6D_5CD_3$, $C_6D_5CH_3$, PhPr, PhEt, cumene, *o*-, *p*-, *m*-xylene, durene, and 1,2,4- and 1,3,5-$Me_3C_6H_3$ [678]. The kinetics of oxidation of fluorene to fluorenone by quinolinium dichromate in DMF containing perchloric acid was studied. The rate of the reaction was first order each in substrate, oxidant and acid. A kinetic isotope effect, $k_H/k_D = 6.0$ was observed. The Hammett-plot gave a value of $\rho = -1.50$. A radical mechanism was proposed with Cr^V intermediate species [679].

The oxidative free-radical cyclization of racemic **273a** by 2 equiv $Mn(OAc)_3 \cdot 2H_2O$ and 1 equiv $Cu(OAc)_2 \cdot H_2O$ in AcOH at 25°C afforded **274a** as a single diastereomer in 44% isolated yield. Enantiomerically pure (*S*)-**273b** gave **274b** as a single enantiomer [680].



273 **274**

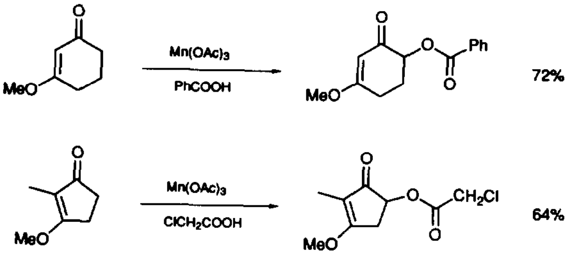
Oxidation of alkyl aryl ketones with $Mn(OAc)_3$ in the presence of carboxylic acids or (*S*)-(+)-10-camphorsulfonic acid gave the corresponding α-acyloxy ketones or α-sulfonyloxy ketone [681]. The synthesis of substituted tetrahydronaphthalenes by Mn^{III}, Ce^{IV}, and Fe^{III} oxidation of substituted diethyl α-benzylmalonates in the presence of olefins was investigated. *E.g.*: the oxidation of **275** by manganese(III) acetate in the presence of 1-octene in acetic acid at 60°C gave 96% conversion and 86% yield of **276** [682].



275 **276**

Similar oxidations between substituted diethyl picolylmalonates and alkenes or alkynes afforded substituted tetrahydro- or dihydroquinolines (and/or isoquinolines), respectively [683].

The α'-oxidation of β-alkoxycyclopentenones and β-alkoxycyclohexenones to α-acyloxy derivatives using manganese(III) acetate in combination with a carboxylic acid was reported [684]. *E.g.*:

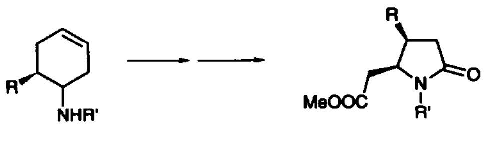


The kinetics and mechanism of oxidation of malonic acid and n-butylmalonic acid by manganese(III) pyrophosphate in aqueous acetic acid + sulfuric acid media were studied [685].

The phase-transfer catalyzed permanganate oxidation of 3 British coals were studied by analyzing the soluble and insoluble oxidation products. The phase-transfer catalyzed permanganate reagent was found to be a milder, more selective oxidant than the conventional basic permanganate reagent and appeared to have potential as a structural probe for coal [686]. The oxidation with $KMnO_4$ in aqueous KOH was used for characterization and classification of kerogen from North Korea oil shale based on its oxidation products [687]. The oxidation of *o*-, *m*-, and *p*-xylene, and 2,3-$Me_2C_6H_3NO_2$ with $KMnO_4$ at 95°C in $PhNO_2$-H_2O containing 2,3,5-triphenyl-tetrazolium chloride as the phase-transfer catalyst afforded benzoic acid derivatives in up to 79% yield [688]. The kinetics of oxidation of 1,3-diethylbenzene by $KMnO_4$ in KOH/H_2O solution to *m*-$HO_2CC(=O)C_6H_4C(=O)CO_2H$ and *m*-$HO_2CC_6H_4C(=O)CO_2H$, and the preparation of these products were studied [689]. Styrene was oxidized at 25–30°C with montmorillonite-$KMnO_4$ in benzene-water to give 91% benzoic acid [690].

RuO_4 oxidation was used for molecular characterization of kerogenes. The mild selective chemical degradation with RuO_4 gave extracts which contained series of straight-chain, C_{9-32} monocarboxylic acids, C_{4-34} α,ω-dicarboxylic acids, C_{11-32} branched mono- and C_{5-28} dicarboxylic acids, C_{14-21} isoprenoid, and C_{30-34} hopanoic acids [691].

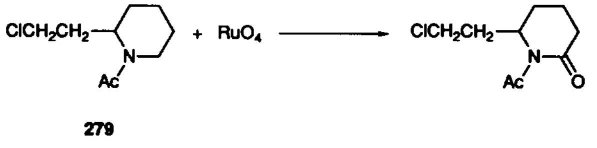
Pyrrolidones **278** were prepared in 10–88% yield by RuO_4 oxidation of **277** [692].



277 **278**

R = H, Me, Et, Ph; R' = Me, $PhCH_2$, Ac, ${}^tBuO_2C$, $PhCH_2O_2C$

The complex $[Ru^VL(O)]^{2+}$ (HL = [2-hydroxy-2-(2-pyridyl)ethyl]bis[2-(2-pyridyl)-ethyl]amine was found to be a very active stoichiometric oxidant towards hydrocarbons. The kinetics and the kinetic isotope effects were studied [693]. The key step in a synthesis was the ruthenium tetroxide oxidation of N-acetyl-2-(2-chloroethyl)piperidine, **279** [694].

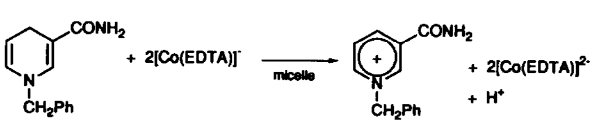


279

The complex *trans*-$[RuLO_2][ClO_4]_2$ (L = N,N'-dimethyl-N,N'-bis(2-pyridyl-methyl)propylenediamine) was found to be a powerful oxidant, capable of oxidizing toluene to benzaldehyde, alcohols to aldehydes (ketones), THF to γ-butyrolactone, and norbornene to *exo*-2,3-epoxynorbornane in high yields at room temperature [695].

The oxidation of cyclohexane and cyclohexanol by $[Ru^V{=}O(EDTA)]^-$ in water + dioxane medium was reported [696]. The kinetics of oxidative dealkylation of diethylamine and triethylamine [697], and the kinetics of oxidations of toluene to benzyl alcohol and benzyl alcohol to benzaldehyde with $[Ru^V{=}O(EDTA)]^-$ were studied spectrophotometrically at constant pH and ionic strength [698].

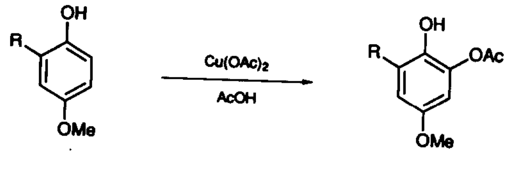
The rate of oxidation of **280** to **281** by ethylenediaminetetraacetato cobalt(III) at pH 9.0 and 30°C was found to be higher in the presence of dodecyltrimethyl-ammonium chloride. Sodium dodecyl sulfate retarded the reaction [699].

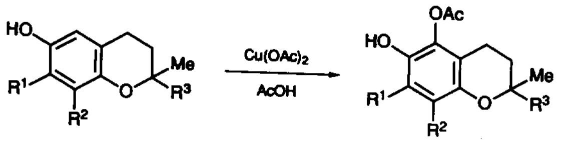


280 **281**

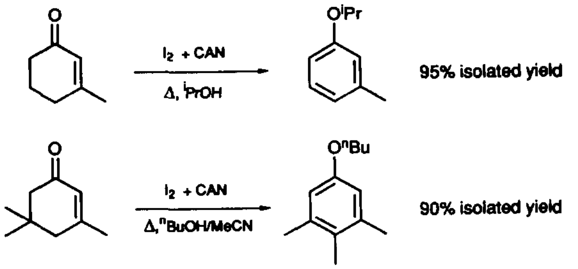
A 3-term rate equation was obtained for the oxidation of styrene by Pd^{II} chloro complexes in aqueous solutions. This indicates that the decomposition of the intermediate styrene-Pd π-complex proceeds by three paths [700]. The oxidation of toluene with hexabromoplatinate ion in trifluoroacetic acid-water solution gave 3,3'-, 3,4'- and 4,4'-bitolyl in a ratio of 2.5 : 27.5 : 70.0, respectively [701]. CF_3CO_2Me was formed in 0.5–5% yield in the oxidation of CH_4 by metal complexes such as $Pt_n(O_2CCF_3)_m$ (n, m = 2, 6; 1, 4; 1, 2) and $Rh(O_2CCF_3)_3$ in CF_3CO_2H [702].

The ligand oxidation of Cu^I and Cu^{II} alcoholates and carboxylates to carbonyl compounds and the selective ortho-hydroxylation of N-benzoyl-2-methylalanine Cu^{II} salt by trimethylamine N-oxide was studied [703]. Oxidation of *p*-methoxy-phenols and 6-chromanols by equimolar amounts of copper(II) acetate in refluxing acetic acid gave the corresponding *o*-acetoxyphenols and 5-acetoxy-6-chromanols in 20–80% yield [704]. *E.g.*:





The oxidation of *o*- and *p*-xylene to methylbenzyl alcohols and then to tolualdehydes by ceric sulfate in sulfuric acid solution were studied. The reactions were first order in xylene and in oxidant [705]. New tetravalent lanthanide salts, such as $Ce(SO_3CF_3)_4$ and Pr_6O_{11} in HCl, were used to oxidize benzyl alcohol, toluene derivatives and other organic substrates to give aldehydes, acids and ketones [706]. The reaction of 2-cyclohexen-1-one derivatives with iodine-cerium(IV) ammonium nitrate (I_2-CAN) in alcohols afforded the corresponding alkyl phenyl ethers in good yields [707]. *E.g.*:



The kinetics of oxidation of 8-hydroxyquinoline and its derivatives by cerium(IV) in acidic medium were investigated [708].

4.6.2. *Epoxidation and dihydroxylation of olefins*

Asymmetric epoxidation of 1,2-divinylethylene glycol isomers with t-butyl hydroperoxide in the presence of a stoichiometric amount of diisopropyl tartrate and $Ti(O^iPr)_4$ and 4Å molecular sieves has been studied [709].

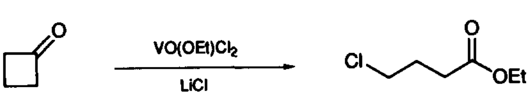
The reactivity of $VO(acac)_2OOR$ (R = $PhCMe_2$ and Me_3C) towards cyclohexene was investigated [710]. Vanadium pentoxide was found to be an efficient catalyst for epoxidation of olefins (*e.g.*: cyclohexene, 1-hexene, *etc.*) with t-butyl hydroperoxide between 45 and 80°C [711].

The selectivity of epoxidation of *cis*- *vs*. *trans*-alkenes by $(Br_8TPP)Cr^V(O)(Cl)$ has been studied [712]. Evidence was provided that a carbocation radical intermediate is formed on oxidation of (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl) ethene by $(Br_8TPP)Cr^V(O)(Cl)$ [713]. The reaction of stigmasterol and pregnenolone with chromyl diacetate in CH_2Cl_2 at −94°C gave the 5β-,6β-epoxy derivatives in 26% and 38% yield, respectively [714].

The effect of anions on the epoxidation of styrene, α-methylstyrene, β-methylstyrene, *p*-chlorostyrene, and *m*-divivylbenzene with H_2O_2 in the presence of ammonium heptamolybdate(VI)-dioctyltin oxide catalyst in $CHCl_3 \cdot H_2O$ was investigated. The presence of Cl^- almost suppressed the oxidation, while no substantial effect was observed in the case of ClO_4^- [715]. Long-chain *rac*-1-*s*-alkylglycerols were prepared by the hydroxylation of alkyl allyl thioethers with cetyltrimethylammonium permanganate in CH_2Cl_2 [716]. See also [695].

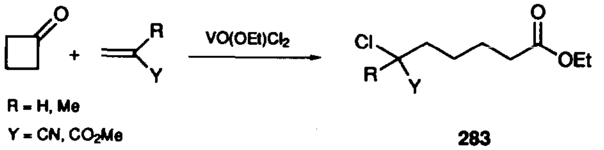
4.6.3. *Oxidation of O-containing functional groups*

The oxidation of cyclobutanone with $VO(OEt)Cl_2$ in ether at room temperature in the presence of LiCl gave **282** in 43% yield.



282

In the presence of an olefin bearing an electron-withdrawing substituent, **283** was formed as the main product in 55% yield [717].



283

The oxidation of NADH with vanadyl ion was investigated. From the results it was concluded that O_2^- is generated as a reaction intermediate during the oxidation of NADH by the V^{IV} ion in the presence of O_2 [718].

The chromium(VI)-isoquinoline compound, $[C_9H_7NH]_2Cr_2O_7$, was found to be an efficient oxidizing agent for the conversion of allyl, primary and secondary alcohols to the corresponding aldehydes or ketones [719]. Poly(vinylpyridine)-supported silver dichromates were found to act as versatile, mild and efficient oxidants for hydroxy compounds, oximes, amines, thiols, and aromatic hydrocarbons [720]. The oxidation of aliphatic and alicyclic secondary alcohols with chromium(VI) trioxide at 40°C in the presence of "wet"-aluminium oxide in hexane afforded the corresponding ketones in excellent yields [721]. Oxidation of deoxy and aminodeoxy sugars with $CrO_3 + Ac_2O +$ pyridine in CH_2Cl_2 gave hexopyranosiduloses in high yields [722]. Cr complexes with formic acid and H_2O were formed in the oxidation of isoamyl acetate by $CrO_2(CMe_3)_2$ in dioxane and ^{t}BuOH [723].

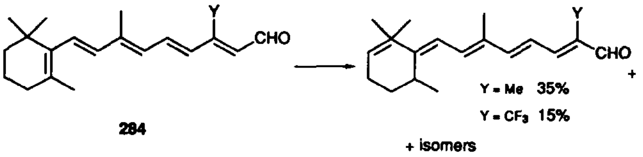
The influence of Mn^{II}, Ce^{III}, Fe^{II}, and Co^{II} sulfates and of complexing ligands such as EDTA, 2,2′-dipyridyl and 1,10-phenanthroline on the kinetics of oxidation of 2-propanol by chromic acid in aqueous medium was studied. The reaction rate constants decrease by the addition of metal ions and increase in the presence of ligands [724]. The influence of sodium dodecyl sulfate (SDS) micelles on the oxidation of alcohols by chromic acid was investigated. The kinetics of the oxidation reaction reveal the catalytic effect of SDS [725]. The kinetics of chromium(VI) oxidation of alkanol components of sodium dodecyl sulfate reverse micelles in perchloric acid medium were studied. A linear dependence of the reaction rate on Cr^{VI} and $HClO_4$

concentration in the aqueous phase and an inverse dependence on the amount of alkanol in the reverse micelles was found [726]. The kinetics of the oxidation of benzyl alcohol by potassium chlorochromate were studied in dimethyl sulfoxide- CH_2Cl_2 medium [727]. The kinetics of the acid-catalyzed pinacol oxidation to acetone by pyridinium chlorochromate was studied. In nitrobenzene-dichloromethane solution the reaction is first order with respect to oxidant and pinacol [728]. The kinetics of oxidation of a number of *ortho*-, *meta*-, and *para*-substituted benzaldehydes to the corresponding benzoic acid by pyridinium fluorochromate, in dimethyl sulfoxide, were studied [729].

Oxidation of 3-methoxy, 3,4-dimethoxy, and 3,4,5-trimethoxybenzaldehyde with Mn^{III} pyrophosphate in acetic acid + sulfuric acid is zero order with respect to oxidant and first order with respect to substrate. Manganese(II) retards the oxidation [730]. The oxidation of primary alcohols by $KMnO_4$ in 3N-H_2SO_4 has been applied in preparation of carboxylic acids [731]:

R = *n*-hexyl, *n*-octyl, *n*-decyl, and C_6F_5

The oxidation of benzaldehydes and $PhCH_2CN$ by $KMnO_4$ under phase-transfer conditions was investigated [732]. An unexpected one carbon elimination during allylic oxidation of **284** by MnO_2 was reported [733].



284

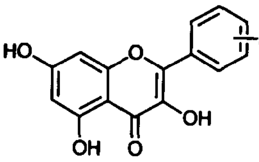
The kinetics of the oxidation of cyclobutanol and substituted mandelic acids by permanganate were studied. The results were best accommodated by a mechanism in which the initial reaction is the addition of a manganese–oxo bond to the α-C–H bond of the alcohol, followed by homolytic cleavage of the resulting Mn–C bond to give free-radical intermediates [734]. The kinetics of oxidation of α- and β-glycerophosphates to the corresponding phosphoglyceraldehyde by MnO_4^- in $HClO_4$ were found to be first order with respect to [glycerophosphate], $[MnO_4^-]$, and $[H^+]$ [735]. The kinetics of the oxidation of tartrate and mesoxalate ion by permanganate ion in strongly alkaline solutions were studied [736].

The deuterium isotope effect in the oxidation of sodium (2-d_2) caproate with $KMnO_4$ in 3 M NaOH has been determined; sodium caproate of natural isotopic composition reacts 1.3 times faster than the deuterium-labeled compound [737]. Activation parameters characterizing the temperature dependence of the deuterium isotope effect in the oxidation of $CH_3CH_2CD_2COO^-$ with manganate in aqueous NaOH solutions have been determined [738].

The kinetics of oxidation of DL-valine by $KMnO_4$ in a concentrated sulfuric acid medium have been studied. Two reaction paths were identified: one which is catalyzed by Mn^{II} and a non-catalyzed path. Permanganic acid is supposed to be the actual oxidizing agent [739]. A kinetic study of the oxidation of L-threonine by MnO_4^- revealed the autocatalytic effect of Mn^{2+} [740]. The oxidation of oxalic acid by permanganate was investigated in order to find an explanation for the oscillatory changes in the absorbancy [741].

The kinetics of the oxidation of a series of benzoins by octacyanomolybdate(V) in a buffered alkaline aqueous-MeOH medium were studied spectrophotometrically. The following order of reactivity was observed: *o,o'*-dichloro- > *p,p'*-dichloro- > *m,m'*-dimethoxybenzoin > benzoin > *p,p'*-dimethoxy > *o,o'*-dimethoxybenzoin [742]. The kinetics of the oxidation of α-hydroxyacids such as mandelic, glycolic, and lactic acid by dodecatungstocobaltate(III) were investigated in the 0-5.4 pH range [743]. The kinetics of oxidation of acetophenone to benzoic acid and formaldehyde by diperiodatonickelate(IV) in the presence and absence of Os^{VIII} were studied [744].

Flavonoids such as **285**, containing 3-OH, 3'-OH, or 4'-OH groups were oxidized by Fe^{3+} ions in acid solution [745].



R = 4-OH, 3,4-$(OH)_2$, 2,4-$(OH)_2$
3,4-$(OH)_2$-5-SO_3H

285

The activity of montmorillonite-supported iron(III) nitrate and copper(II) nitrate was investigated in oxidation of aromatic alcohols to carbonyl compounds. It was established that, in contrast to literature data, even the less stable iron reagent can be stored for weeks without substantial loss of activity [746].

The kinetics of the oxidation of catechols and 2-methyl-1,4-dihydroxybenzene by iron(III) tetracyano 2,2-bipyridyl ion in aqueous solution were studied by stopped-flow spectrophotometry in the pH range 2.5-6 [747]. The kinetics of the oxidation of L-ascorbic acid by hexacyanoiron(III) in acidic aqueous solution was investigated as a function of pH, temperature and pressure. The activation parameters support the operation of an outer-sphere electron-transfer mechanism [748,749].

The oxidation of dihydroxy aromatic substrates by hexachloroiridate(IV) was studied kinetically in aqueous perchloric acid solution at pressures up to 1000 bar. The volumes of activation were found to be in the range of -20 to -30 cm^3 mol^{-1} [750]. DL-α- and DL-β-glycerophosphates were oxidized by $[IrCl_6]^{2-}$ in a NaOAc + AcOH buffer to give the corresponding phosphoglyceraldehydes. A mechanism was suggested [751].

α-Glycerophosphate and β-glycerophosphate was oxidized by osmium(VIII) in alkaline medium in a one-step two-electron transfer process leading to the formation of 3-phosphoglyceraldehyde and 2-phosphoglyceraldehyde, respectively [752]. The kinetics of OsO_4-catalyzed oxidation of cyclopentanol, cyclohexanol, and cyclooctanol to the corresponding ketone by alkaline hexacyanoferrate(III) were studied [753].

The mechanism of oxidation of L-sorbose, D-galactose, D-xylose, and L-arabinose in aqueous alkaline medium by osmium tetroxide was studied using the stopped-flow technique in kinetic measurements. Based on the experimental results the formation of an activated complex between enediol and OsO_4, which slowly decomposed into Os^{VI} species and intermediate products, was suggested [754].

Ethanol was oxidized by $[(mes)OsCl_2]_n$ (mes = 1,3,5-trimethylbenzene) at 80°C in the presence of 3,3-dimethyl-1-butene forming $[(mes)OsH(CH_3)CO]$ in up to 56% yield [755].

Oxidation of aliphatic aldehydes with Os^{VIII} in alkaline solution is first order in both aldehyde and Os^{VIII}. Separate rate constants for the oxidation of hydrate and free aldehyde forms have been evaluated and the aldehyde hydrate was postulated as the active reductant [756].

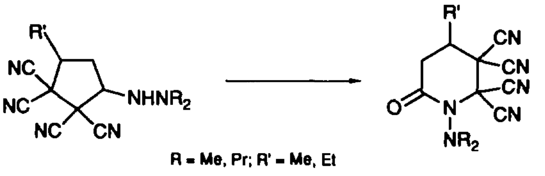
An insoluble copper derivative obtained from Cu^{II} ion and H_2O_2 in slightly acidic water was found to be a versatile oxidizing reagent for *e.g.*: alcohols, phenylacetic acids, primary amines, triphenylphosphine, and toluene [757]. The oxidation of DL-mandelate to benzaldehyde by $[Ag(OH)_4]^-$ in strongly alkaline media was studied by stopped-flow spectrometry. A base-catalyzed process, followed by C–C bond cleavage, was found to be the most probable way of decarboxylation [758].

Micellar catalysis in the oxidation of acetophenones by cerium(IV) was studied by kinetic methods. The rate data were rationalized on the basis of a reaction between the acetophenones on the micelle surface and active Ce^{IV} species in the bulk aqueous phase [759]. The kinetics of oxidation of hydroquinone by Ce^{IV} showed first order with respect to each of the reactants. A free radical mechanism was proposed [760]. The kinetics of oxidation of *o*-, *m*-, and *p*-methoxy substituted mandelic acids to the corresponding benzaldehydes by Ce^{IV} were studied spectrophotometrically. A fast preequilibrium complexation between Ce^{IV} sulfato species and methoxy-substituted mandelic acids, and a rate-determining decarboxylation were suggested [761]. The main product of allyl alcohol oxidation by cerium(IV) in aqueous acid was found to be acrolein in the osmium(VIII)-catalyzed reaction and acrylic acid in the palladium(II)-catalyzed reaction. The kinetics of these reactions were studied [762]. Oxidation of *p*-nitrophenol by Ce^{IV} gives *p*-nitro-2-benzoquinone. The reaction is first order in both substrate and oxidant; disproportionation of the complex between the two reactants is the rate-determining step [763].

4.6.4. Oxidation of N-containing organic compounds

Oxidation of acetanilide with vanadium(V) was found to be first order in oxidant, the order in acetanilide varied from one to zero [764]. The kinetics of oxidation of malathion by pyridinium chlorochromate in a chlorobenzene-nitrobenzene mixed solvent have been reported. A 1 : 2 stoichiometry was observed [765].

The kinetics and mechanism of the oxidation of iminodiacetate, nitrilotriacetate, and ethylenediaminetetraacetate by *trans*-cyclohexene-1,2-diamine-N,N,N′,N′-tetraacetatomanganate(III) in aqueous media were studied. All reactions were found to be first order both in complex and reductant concentration [766]. A kinetic study revealed that the permanganate oxidation of triethylamine in aqueous phosphate buffers is autocatalytic. A soluble form of colloidal manganese dioxide temporarily stabilized in solution by adsorption of phosphate ions on its suface were identified as the catalyst [767]. The oxidation of imines with potassium permanganate was investigated. In acetonitrile-water the corresponding amide was the major product in reasonable yields [768]. The oxidation of **286** with $KMnO_4$ in the presence of HCl afforded **287** in 40–57% yield [769].

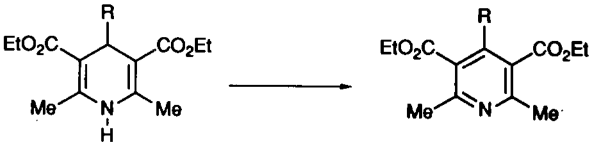


286 **287**

The kinetics of the $KMnO_4$-oxidation of ethylenediaminetetraacetic acid to ethylenediamine-N,N′,N′-triacetic acid and CO_2 in acidic media were investigated [770].

The oxidation of the essential amino acids by ferrate(VI) and ferrate(V) were studied by stopped-flow and pulse radiolysis technique at pH 12.4 and 23–24°C. Both hypervalent iron species react preferentially with the protonated forms of amino acids, and in the absence of dioxygen, the oxidation proceeds by chain reactions in which amino acid free radicals and Fe^V are the chain carriers [771]. The kinetics of oxidation of arylhydrazides, $XC_6H_4CONHNH_2$ ($X = H$, *p*-Cl, *p*-Me, and *o*-NO_2) by alkaline hexacyanoferrate(III) were studied. The reactions are first order in both oxidant and substrate, and fractional order in $[HO^-]$ [772]. The kinetics of oxidation of tyrosine by alkaline $K_3Fe(CN)_6$ were studied. The rate was first order in both substrate and oxidant, but independent of the concentration of alkali [773]. The kinetics of oxidation of glutamic acid and aspartic acid by alkaline hexacyano-ferrate(III) to give the corresponding α-keto acid was investigated. The reaction was found to be first order in both substrate and oxidant, but is independent of the concentration of alkali. A slow C–H bond breaking was correlated with the observed value of $k_H/k_D = 8.1–8.3$ [774]. Oxidation of phenylhydrazine or (*p*-bromophenyl)hydrazine by $[Fe(CN)_6]^{3-}$ is first order in both hydrazine and oxidant. Benzene and bromobenzene are the oxidation products [775]. The kinetics of oxidation of amino acids by hexachloroiridate(IV) in aqueous acid medium were studied [776].

Montmorillonite supported $Cu(NO_3)_2$ in CH_2Cl_2 at room temperature combined with sonication was used to oxidize **288** to **289** [777].

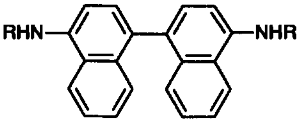


288 **289**

R = Ph, 4-ClC_6H_4, 3-$O_2NC_6H_4$, 4-$O_2NC_6H_4$

The kinetic and mechanism of the multi-step oxidation of ethylenediamine-tetraacetate ion by tetrahydroxyargentate(1 –) in alkaline media were studied [778]. The kinetics and mechanism of oxidation of triethanolamine by diperiodato-argentate(III) anion was studied in aqueous alkaline medium by conventional spectrophotometry [779].

The kinetics of oxidation of *o*-(salicylideneamino)-benzoic acid and *o*-(salicylidene-amino)thiophenol by cerium(IV) in acidic medium were studied. The observed kinetics were interpreted in terms of an initial Schiff base-Ce^{IV} complexation, with subsequent rate-determining decomposition to products [780]. Oxidation of some *p*-phenylenediamine derivatives by Ce^{IV} in aqueous solutions of perchloric acid has been studied. It was shown, that derivatives of *p*-benzoquinone can be obtained on a preparative scale [781]. The mechanism and kinetics of oxidation of **290** with cerium(IV) sulfate in aqueous solutions of sulfuric acid were studied [782].



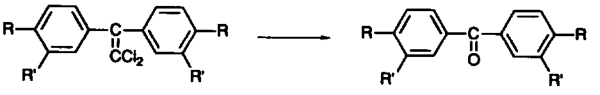
R = Me, Et

290

See also [697].

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

Chlorinated and sulfonated derivatives of benzophenone (**292**; R,R′ = Cl; R = Cl, R′ = SO_3Na; R,R′ = SO_3Na) were prepared by the oxidation of the corresponding 1,1-dichloro-2,2-diaryl compounds (**291**) with CrO_3 in AcOH or with $KMnO_4$ [783].

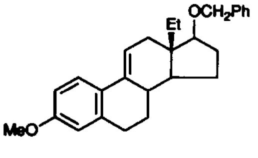


291 **292**

Oxidation of sulfides by barium permanganate in refluxing acetonitrile gave sulfoxides in good yields. Thus, oxidation of $PhSCH_2Ph$ gave 88% of the corresponding sulfoxide [784].

In a study of the oxidation of (arylthio)acetic acids by permanganate ion a new mechanism of the sulfoxide formation was suggested with the involvement of manganate(V) as an intermediate [785]

Oxidation of the product of 9(11)-estratetraenes **293** and BH_3 with a solution of $Na_2Cr_2O_7$ in 20% H_2SO_4 afforded mainly **294** and some **295** and **296** [786].



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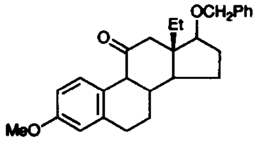

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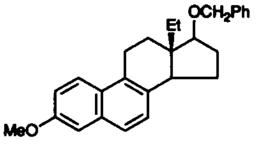

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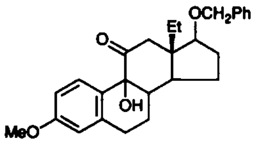


296

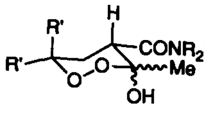
The kinetics of picolinic acid-catalyzed chromium (VI) oxidation of alkyl aryl and diphenyl sulfides were studied in aqueous AcOH. The oxidation was found to be first order each in oxidant, sulfide, and catalyst, at constant $[H^+]$ and ionic strength [787]. The kinetics of oxidation of thioglycollic acid, thiolactic acid, and thiomalic acid by pyridinium chlorochromate [788] and pyridinium fluorochromate [789] to the corresponding disulphides were studied using a stopped-flow technique. The oxidation of DMSO by chromic acid was studied in perchloric acid medium [790]. The kinetics of the oxidation of aryl methyl sulfides to sulfoxides with pyridinium dichromate was studied in aqueous acetic acid. The experiments support the rate equation, $v = k[\mathrm{MeSAr}][\mathrm{oxidant}]$. Decomposition of the complex formed between the sulfide and oxidant was assumed as the rate-determining step [791].

Alkoxyaryl compounds were obtained in 55–82% yield from arylpalladium complexes in alcohol solution by reaction with $Mo(O_2)_2(=O)(H_2O)(HMPT)$ [792]. The kinetics of the oxygen transfer between *cis*-$MoO_2(R_2dtc)_2$] (R = Me, Et, ${}^iPr$, ${}^iBu$, Bz, Ph; dtc = dithiocarbamato) and PPh_3 were studied. A correlation between the rate constants and the formal potentials of $[MoO_2(R_2dtc)_2]^{0/-1}$ was found [793].

A series of thiophene oligomers were oxidized in diluted solution by stoichi-ometric amounts of $FeCl_3$ to generate the corresponding radical cations [794]. The oxidation of monomolecular films of 1-octadecanethiol to dioctadecyl disulfide by potassium hexacyanoferrate (III) was examined [795].

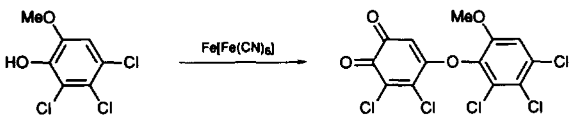
4.6.6. Oxidative coupling reactions

A mixture of carbamoyl-3-methyl-1,2-dioxan-3-ols (**297**) were formed in good yields in the reactions of 1,1-disubstituted ethenes with acetamide or N-substituted acetoamides and O_2 in the presence of $Mn(OAc)_3$ at room temperature. Similar reactions were found with Mn^{II}, Co^{II}, and Co^{III} acetates [796].



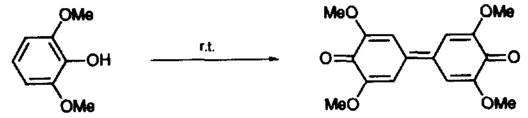
297

The oxidative coupling of **298** by $Fe[FeCN)_6]$ at room temperature gave **299** in > 90% yield [797].



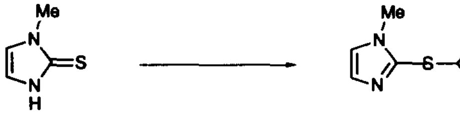
298 **299**

The oxidation of 2,6-disubstituted phenols with cobalt(III) acetate in acetic acid gave the corresponding diphenoquinones in excellent yields [798]. *E.g.*:



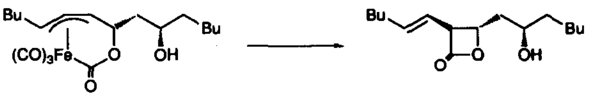
2,2′-Bisquinones were prepared from stannylquinones at room temperature in the presence of $(PPh_3)_2PdCl_2$ and CuI as the catalyst and 1,4-benzoquinone as the stoichiometric oxidant [799]. *E.g.*:

The oxidation of **300** to **301** by copper(II) perchlorate or nitrate in nitromethane solution was investigated. Evidence showed that the sulfur extruded from **300** during the formation of **301** was ultimately oxidized to the sulfate ion [800].



300 **301**

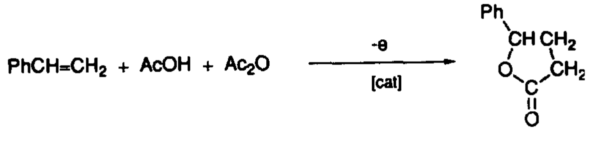
The oxidation of **302** by cerium ammonium nitrate in ethanol afforded **303** with 26% yield [552].



302 **303**

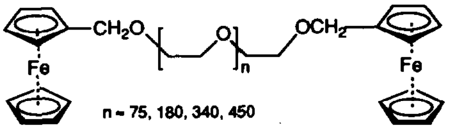
4.7. Electrooxidation and photooxidation

Selective electrooxidation of various primary and secondary alcohols to the corresponding aldehydes or ketones by the Cr^{VI}/Cr^{III} system under phase-transfer catalysis was investigated [801]. The electroassisted oxidation of *cis*-cyclooctene to epoxide and of adamantane to adamantanone by molecular oxygen, catalyzed by polypyrrole manganese porphyrin films at room temperature, has been studied. Up to 100 turnovers of the catalyst per hour were observed for a substrate/catalyst ratio of 1500 [802]. Small amounts of Mn $(OAc)_3 \cdot H_2O$ facilitate the carboxymethylation of styrenes to γ-butyrolactones in AcOH + Ac_2O solution during anodic oxidation [803]. *E.g.*:



80% yield

Water-soluble polyethyleneglycol-bound ferrocenes **304** were used as redox catalysts in a continuous electrochemical activation of flavoenzimes for the enzyme-catalyzed oxidation of *p*-cresol to *p*-hydroxybenzaldehyde [804].

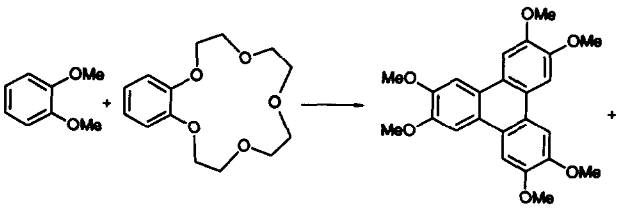


304

The electrocatalytic oxidation of ascorbic acid was studied using among others a polyvinylferrocene-modified microdisk electrode. The catalytic reaction rate constants were determined [805]. The indirect anodic oxidation of 2-methylnaphthalene to 2-methylnaphthoquinone in an undivided cell using platinum electrodes in the presence of ruthenium compounds as catalysts has been studied. $RuCl_3 \cdot 3H_2O$ was found to be the most efficient catalyst [806]. The electrochemical oxidation of benzyl alcohol, isopropanol and THF was studied in the presence of Ru^{VI} complexes as the catalysts [807].

The electrooxidation of glutathione on graphite electrodes modified with preadsorbed vitamin B_{12} (cobalamin), Co phthalocyanine and Co tetrasulfophthalocyanine was studied. The catalytic activity of the complexes decreased in the stated order. A mechanism was proposed [808]. Electrochemically generated Co^{3+} in acetic acid was used for oxidation of toluene to benzyl acetate [809].

Platinum cluster-derived electrodes from metal carbonyl complexes were tested for the electrocatalytic activity for the anodic oxidation of methanol. Particularly the Pt_{15}-derived electrodes were found to be highly active [810]. Platinized-titanium electrodes were found to be highly active electrocatalysts for urea oxidation [811]. The platinized titanium surfaces were as much as 1900 times more active for urea oxidation than smooth platinum surfaces on a per unit mass of Pt basis [812]. Mixtures of triphenylenes such as **305** and **306** were prepared by anodic oxidation of the corresponding mixtures of aromatic *ortho*-diesters using a platinum working electrode [813].



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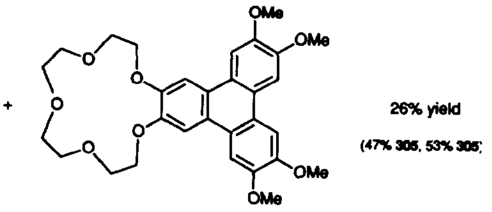

306

Photooxidation of hexane by polyvanadate in CF_3COOH afforded isomeric trifluoroacetates and carbonyl compounds; the reactivity order of the H atoms of hexane was 1 : 2.9 : 0.43 in positions 3, 2, and 1, respectively [814]. In photochemical oxygenation of cyclohexane by $KVO_3 + CF_3COOH$ or $K_2Cr_2O_7 + Bu_4NBr + H_2O + CH_2Cl_2$ in air, the source of oxygen atoms in the product cyclohexanol and cyclohexanone was found to be air dioxygen rather than a metal oxo-complex [815].

The photooxygenation of cyclohexene with air in the presence of $CrCl_3 + PhCH_2NEt_3Cl$ as the catalyst afforded mainly cyclohexanone and showed in the case of C_6D_{12} a 2.9 times slower conversion than with C_6H_{12} [816]. The photooxygenation of cyclohexane by air oxygen in CH_2Cl_2 in the presence of $(Bu_4N)_2CrO_4$ or $(Bu_3SnO)_2CrO_2$ was studied. An increased rate of cyclohexanol and cyclohexanone formation was obtained by the addition of PhIO [817]. The oxidation of cyclohexane and alkylaromatic compounds with CrO_3 in acetonitrile under irradiation was studied. Cyclohexane gave a mixture of cyclohexanone and cyclohexanol, while toluene and styrene gave benzaldehyde. Ethylbenzene gave 53% benzaldehyde and 11% 1-phenylethanol [818].

Photooxidation of cyclohexane in acetonitrile solution in the presence of catalytic amounts of $FeCl_3$ afforded alcohols and carbonyl compounds. In the presence of $FeBr_3$ ethylbenzene was converted to 1-phenylethanol, acetophenone and benzaldehyde [819]. Copper halides showed similar activities [820]. Photochemical oxygenation of cyclohexane, ethylbenzene, and styrene with air oxygen in acetonitrile solution using $[(\pi\text{-ArH})Fe(\pi\text{-}C_5H_5)]^+BF_4^-$ (ArH = benzene, toluene) as the catalyst precursor was reported [821]. Photocatalytic oxygenation of strained alicyclic alkanes with μ-oxo-bis[tetraphenylporphyrinatoiron(III)] and molecular oxygen resulted epoxidized and/or hydroxylated products depending on the structure of the alkene [822]. The photocatalytic oxidative cleavage of 1,2-diols by air in the presence of [*meso*-tetrakis(3,5-dichloro-1-methyl-4-pyridiniumyl)porphyrinato]iron(III), and [*meso*-tetrakis(1-methyl-4-pyridiniumyl)porphyrinato]-iron(III) was studied [823]. The air oxidation of cyclohexane to cyclohexanone at 22°C was achieved in the presence of catalytic amounts of iron(III) complexes of *meso*-tetrakis(2,6-dichlorophenyl)-porphyrin under irradiation with light of wavelength between 350 and 450 nm [824]. Norbornene oxide was produced in 48% yield together with diethyl sulfoxide (90%) and diethyl sulfone (5%) under 1 bar O_2 and irradiation from a reaction mixture of norbornene, diethyl sulfide, tetraphenylporphyrine and a catalytic amount of (tetrakis(pentafluorophenyl)porphyrinato)iron(III) chloride [825].

The kinetics and mechanism of the photo-induced oxidation of ascorbic acid by O_2 to dehydroascorbic acid and H_2O_2 catalyzed by ruthenium(II) complexes containing 2,2′-bipyridine and 2,2′-bipyrazine were studied [826].

The photooxidation of formaldehyde, acetaldehyde, propionaldehyde, acetone, methyl ethyl ketone, and diethyl ketone by hexachloropalladate(IV) and iridate (IV) ions were reported [827].

The complex $[Pt_2(\mu\text{-C=CHPh})(C{\equiv}CPh)(PEt_3)_3X]$ or $[Pt_2(\mu\text{-C=CHPh})(PEt_3)_3X_2]$ was found to induce the photocatalytic oxidation of 2-propanol to acetone and H_2 [828]. Trichlorocuprate(II) ions act as catalyst in the photogeneration of H_2 from aqueous solutions of acetic acid in the presence of HCl [829]:

$$CH_3COOH + 2H_2O \xrightarrow[h\nu]{CuCl_3^-} 2CO_2 + 4H_2$$

See also [486].

5. Reviews

Organometallic compounds in synthesis and catalysis. 106 refs. [830].

Homogeneous transition metal catalysis in oleochemistry. 243 refs. [831].

Homogeneous catalysis by transition metal complexes. 311 refs. [832].

Transition metal complex catalysts and biocatalysts chemically bonded to inorganic supports by means of silyl-substituted anchoring ligand. 95 refs. [833].

Ab initio MO studies of elementary catalytic reactions and catalytic cycles in connection, among others, with olefin hydrogenation and hydroformylation. 110 refs. [834].

The various industrial processes for the manufacture of a variety of bulk and fine chemicals were reviewed and compared. 22 refs. [835].

The use of supported liquid-phase catalysts in fluidized-bed reactors. Transition metal complex-catalyzed hydroformylation of propene. 10 refs. [836].

Electrochemical syntheses involving carbon dioxide (MeOH synthesis, carboxylations). 123 refs. [837].

Advances in catalytic carbonylation with transition metal complexes in homogeneous phase. 244 refs. [838].

Carbon monoxide activation by homogeneous catalysts. 152 refs. [839].

Industrial application of carbon monoxide chemistry for the production of speciality chemicals. 104 refs. [840].

Dihydrogen complexes of metalloporphyrins: characterization and hydrogen-transfer reactivity. A review with commentary and 12 refs. based on the research of J.P. Collman, *et al.*, (1990). [841].

An account about the parahydrogen-induced polarization in connection with different homogeneous hydrogenation catalysts ($RhCl(PPh_3)_3$, $RhH_2Cl(PPh_3)_3$, $Rh(COD)(dppe)^+$, $RuHCl(PPh_3)_3$, $RuH_4(PPh_3)_3$, and $Ru(BINAP)(OAc)_2$). 33 refs. [842].

Hydrogen-atom transfer reactions of transition metal hydrides. > 69 refs. [843].

Metal–hydrogen bond cleavage reactions of transition metal hydrides: hydrogen atom, hydride, and proton transfer reactions. 54 refs. [844].

The design of ultraselective rhodium- and ruthenium-phosphine asymmetric hydrogenation catalysts. 3 refs. [845].

Asymmetric catalytic hydrogenation and hydrogen transfer reactions of various functionalized olefins and ketones by use of BINAP-Ru^{II} and BINAP-Rh^{I} complexes. 55 refs. [846].

Asymmetric hydrogenation of (*Z*)-enamides, unsaturated monocarboxylic acids, (homo)allyl alcohols, α-amino ketones, and β-functionalized ketones in the presence of (BINAP)-ruthenium diacetate. 11 refs. [847].

Development of new catalysts for asymmetric transformations and their application to the synthesis of biologically active organic compounds. A review with 29 refs. on the author's studies on the asymmetric hydrogenation of functionalized enamines, ketenes, and α,β-unsaturated carboxylic acids with 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl-ruthenium(II) complexes and the application of this method to the syntheses of biologically active compounds. [848].

Catalytic enantioselective hydrogenation of ketones and imines using platinum metal complexes. 64 refs. [849].

Homogeneous catalytic hydrogenation of aromatic hydrocarbons and heteroaromatic nitrogen compounds: synthetic and mechanistic aspects. 36 refs. [850].

Transition-metal-promoted hydroborations of alkenes. 65 refs. [851].

Reductions and deoxygenation of organoheteroatom oxides (sulfones, sulfoxides, phosphine oxides, amine oxides, and organotin oxides) by SmI_2. 51 refs. [852].

The transition metal catalyzed methane dehydrogenation and oxidation. 19 refs. [853].

Carbonyl and thiocarbonyl-chlorobis(trialkyl- andtriarylphosphine)rhodium(I)-catalyzed photodehydrogenation of alkenes and alcohols. 29 refs. [854].

A review with commentary of T. Mukaiyama's research on nickel(II) complex-catalyzed epoxidation of olefins with molecular oxygen and primary alcohol. 10 refs. [855].

The research of W. Nam, Y. Yang, F. Diederich, and J.S. Valentine (1990) about epoxidation of olefins by iodosylbenzene in the presence of Zn^{II}/Al^{III} and Fe^{III}/Al^{III} complexes was reviewed with commentary. 12 refs. [856].

The catalytic enantioselective epoxidation of unfunctionalized olefins. 11 refs. [857].

Enantioselective epoxidation of unfunctionalized olefins catalyzed by (salen)manganese complexes. 6 refs. [858].

Asymmetric epoxidation with emphasis on the Sharpless epoxidation of allylic alcohols. 242 refs. [859].

Improvement and application of Sharpless reagents in asymmetric epoxidation of allylic alcohols. 31 refs. [860].

Catalytic epoxidation by metalloporphyrin complexes focusing of asymmetric epoxidation. 35 refs. [861].

The research of J.T. Groves and P. Viski on asymmetric hydroxylation, epoxidation, and sulfoxidation catalyzed by vaulted binaphthyl metalloporphyrins was reviewed with commentary. 11 refs. [862].

A review with 17 refs. on asymmetric epoxidation of allylic alcohols using $Ti(O^iPr)_4$ and dialkyl tartrate. Asymmetric dihydroxylation of olefins with OsO_4 and optically active amines as ligands was also described. [863].

Recent developments in asymmetric transition metal-catalyzed epoxidation and dihydroxylation of olefinic compounds. 37 refs. [864].

Asymmetric dihydroxylation of olefins with OsO_4-chiral N,N'-disubstituted-2,2'-bipyrrolidine complexes. 3 refs. [865].

Dioxygen activation and homogeneous catalytic oxidation. Proceedings of the 4th international symposium on dioxygen activation and homogeneous catalytic oxidation. [866].

Metal-complex catalysis of oxidative reactions: principles and problems. 121 refs. [867].

Transition metals as catalysts of "autoxidation" reactions. 97 refs. [868].

Homogeneous palladium(II)-mediated oxidation of methane by hydrogen peroxide under mild conditions. 40 refs. [869].

The selective functionalization of saturated hydrocarbons: Gif and all that. > 35 refs. [870].

Catalytic oxygenation of alkenes by phosphino-complexes of rhodium and ruthenium. 24 refs. [871].

Oxidation of alcohols and diols by MoO_5(PICO) (PICO = picolinate N-oxido anion). 7 refs. [872].

Titanium-promoted enantioselective oxidation of thioethers and synthetic applications. > 20 refs. [873].

Chromium(VI) agents supported on silica gel, other inorganic carriers, or polymers and their application in selective oxidation of alcohols. 42 refs. [874].

Mechanism of oxidation using the metalloporphyrin–PhIO system. 5 refs. [875].

Multiple mechanistic pathways in the oxidation of organic substrates by peroxometal complexes. 11 refs. [876].

Polyoxometallates of V, Nb, Ta, Mo and W as homogeneous oxidation catalysts of alkenes and aromatic compounds. 63 refs. [877].

Kinetics and mechanism studies in biomimetic chemistry: metalloenzyme model systems. A review of mechanistic chemistry of biologycal transport and utilization of O_2 with 125 refs. [878].

Transition metal complexes as catalysts of electrode reactions. 157 refs. [879].

6. List of abbreviations

acac	acetylacetonate
bdpp	2,4-bis(diphenylphosphino)pentane
BINAP	see Fig. 52 and 90
BPPM	see Fig. 2
bpy	2,2'-bypyridine
CHIRAPHOS	see Fig. 56 and 92
$_c$Hx	cyclohexyl
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl, η^5-C_5H_5
Cp*	pentamethylcyclopentadienyl, η^5-C_5Me_5
dba	dibenzylideneacetone
DIOP	see Fig. 1
DIPAMP	see Fig. 58
dippe	1,2-bis(diisopropylphosphino)ethane, $^iPr_2PCH_2CH_2P^iPr_2$
dippp	1,3-bis(diisopropylphosphino)propane, $^iPr_2PCH_2CH_2CH_2P^iPr_2$
DMA	N,N-dimethylacetamide
DMF	N,N-dimethylformamide
DMSO	dimethyl sulfoxide
dppb	1,4-bis(diphenylphosphino)butane, $Ph_2P(CH_2)_4PPh_2$
dppe	1,2-bis(dipheylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$
dppm	bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$

ee	enantiomeric excess
HMPA	hexamethylphosphoric triamide
NBD	norbornadiene
NORPHOS	see Fig. 55
Pc	phthalocyanato
PPN	bis(triphenylphosphine)iminium cation, $(Ph_3P)_2N^+$
py	pyridine
r.t.	room temperature
salen	N,N′-bis(salicylidene)-ethylenediaminato, see Fig. 260
TMP	*meso*-tetramesitylporphinato
TPP	*meso*-tetraphenylporphinato
Ts	*p*-toluenesulfonyl

7. Metal index

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