TRANSITION METALS IN ORGANIC SYNTHESIS: HYDROFORMYLATION, REDUCTION AND OXIDATION

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CONTENTS

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*See also the article by L.S. Hegedus, p. 119; Previous review see J. Organometal. Chem., 237 (1982) 231-450.

Introduction

This review is a continuation of the chapters Hydroformylation, Oxidation and Reductions of the earlier Annual Surveys "Transition Metals in Organic Synthesis" compiled by L.S.Hegedus. The division of the area into two parts has been necessitated not only by the steadily increasing amount of information but also by the fact, that the research done in the field covered by this review is less preparative in character and is dominated by investigations of mechanisms and catalysts. Accordingly the papers in this survey are to a large part grouped by the transition metal complexes used in the organic transformations since the reader may be mainly interested in the transformations taking place within the coordination sphere of the metal.

In accord with the title of the review reductions and oxidations of transition metal complexes which are not accompanied by an organic reaction have been excluded. Data from the patent literature have not been included either, since they usually do not contain information of the organometallic chemistry of the reactions. Oxidative transformations which lead to new carbon-carbon bonds or to heterocycles can be found in the survey of L.S.Hegedus.

I. Theoretical Calculations and General

The mechanism of oxidation and hydrogenation of CO and C_2H_4 on Pd and Pt catalysts was analyzed using the PMO method [1]. The n/i-aldehyde ratio was studied in the hydroformylation of propene with $HCo(CO)_4$ as catalyst by EHMO calculation [2]. Ab initio LCAO-MO-SCF calculations have been performed for the reaction

$$H_2RhCl(PH_3)_2(C_2H_4) \longrightarrow HRhCl(PH_3)_2(Et)$$

This reaction stands as a model for the first H transfer in the dihydrido olefinic intermediate involved in the $Rh(PPh_3)_3Cl$-catalyzed hydrogenation of olefins [3]. Based on MO calculation an outer sphere H-migration mechanism is proposed for the initiation step in the catalytic oxidation of toluene by Co-O_2 complexes. In agreement with experiment, $CoBr_4^{2-}$ appears to be a more effective catalyst for oxidation of methyl aromatics than $CoCl_4^{2-}$ [3a].

Treating metal oxide particles with a mixture of carboxylic acids results in hydrocarbon-miscible metal oxide core particles which are coated with a layer of hydrophobic carboxylates. Co and Mn oxide particles were used in oxidations of cyclohexene, toluene and xylenes. The Co oxides were also used in the hydroformylation of 1-pentene and Ni oxide catalysts were tested in hydrogenations of olefins and aromatic compounds [4].

II. Hydroformylation and Related Reactions of CO

1. Hydrogenation of CO to Hydrocarbons

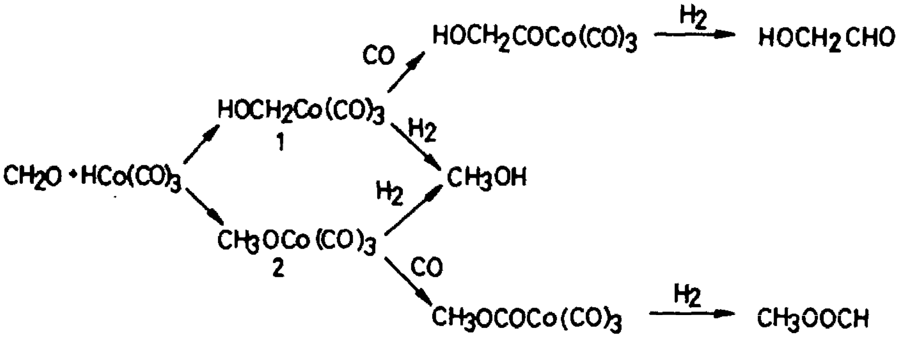
Catalysts prepared from $Co(acac)_2$ and $Mn(acac)_2$ with $AlEt_3$ have been used for the synthesis of C_{2-6} alkenes by CO hydrogenation at 200° in o-terphenyl as solvent [5]. The reaction of H_2 and CO at 180°C with toluene solutions of $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$ produced CH_4 in very low yields. In the presence of $P(OMe)_3$, both clusters catalyzed the formation of CH_4 with significantly higher yields, the methane was, however, derived largely from the phosphite methyl groups [6]. In the low-temperature liquid-phase methanation of carbon monoxide Cp_2VCl_2 and Cp_2NbCl_2 gave 90-95% CH_4 and 5-10% C_2-C_3 hydrocarbons, and formed $>$100 mols CH_4 per metal atom [7].

Fischer-Tropsch catalysis using polystyrene-supported $CpCo(CO)_2$ resulted in predominantly CH_4 production. In an attempt to produce a homogeneous analog of the resin-bound catalyst $CpCo(CO)_2$ dissolved in octane decomposed at 190° without producing hydrocarbons [8]. Supported Os catalysts were prepared by contacting a refluxing n-octane solution of $Os_3(CO)_{12}$ with γ-Al_2O_3, SiO_2 or ZnO. The resulting surface species were characterized as trinuclear complexes by IR spectroscopy. When heated to 100-400° mononuclear Os carbonyl species were formed which catalyzed the conversion of $CO + H_2$ to CH_4 and the hydrogenation of ethylene [9]. A catalyst prepared by the reaction of $Os_3(CO)_{12}$ with a MgO surface exhibited IR spectra suggestive of the formation of the supported cluster $[HOs_3(CO)_{10}OMg\leftarrow]$. The catalyst was active for CO hydrogenation; the products at low conversions were C_1-C_4 paraffins [10].

The catalytic hydrogenation of CO in a NaCl + $AlCl_3$ melt using $Ir_4(CO)_{12}$ as catalyst precursor at 170-180°C yields C_1-C_8 alkanes and cycloalkanes, the major products are isobutane and propane. The $Ir_4(CO)_{12}$ is converted to new Ir carbonyl complexes under the reaction conditions, these decompose irreversibly in the absence of a CO + H_2 mixture [11]. CO is hydrogenated with $Os_3(CO)_{12}$ as a catalyst precursor and BBr_3 as a solvent, catalyst promoter and ultimate reactant at 180°C and 2 atm to C_1-C_5 alkanes and C_1-C_4 alkyl bromides. The major products were MeBr and EtBr. During the course of the catalytic reaction $Os_3(CO)_{12}$ was converted to $Os_2(CO)_6Br_4$. Substitution of BCl_3 for BBr_3 gave an analogous system, but only hydrocarbons were produced [12]. Rh_nL_m+$AlBr_3$+Al catalysts [Rh_nL_m = $Rh_4(CO)_{12}$, $Rh_2(CO)_4Cl_2$, $Na_2[Rh_{12}(CO)_{30}]$, $Rh(PPh_3)_3Cl$ or $Rh(CO)(PPh_3)_2Cl$] were found effective for the synthesis of C_1-C_4 hydrocarbons from CO and H_2. The most effective catalysts was $Rh_4(CO)_{12}$ + $AlBr_3$ + Al which gave at 150° the following products (vol.%): CH_4(47); , C_2H_6(8), C_3H_6(14), i-butane(30), and n-butane(1) [13]. In the Fischer-Tropsch synthesis of aliphatic hydrocarbons over $Rh_4(CO)_{12}$ + $AlBr_3$ + reducing agent catalytic systems, the systems containing Mg or Al as reducing agent showed the highest catalytic activities [14]. Reduction of CO by $LiAlH_4$ containing $Cp_2Fe_2(CO)_4$ yielded C_1-C_4 hydrocarbons in ≈40% combined yield [15].

2. Hydrogenation of CO to Oxygen-containing Organic Compounds

Investigation of different cobalt carbonyl complexes as possible catalyst precursors for CO hydrogenation to CH_3OH (and higher alcohols) at 180-200°C and 200 atm in p-dioxane solution indicated that only complexes which generate $HCo(CO)_4$ under the reaction conditions are active as catalysts. $Ru_3(CO)_{12}$ (which is transformed to $Ru(CO)_5$ as the major component) is slightly more active for CO hydrogenation that the Co systems but it is completely inactive for the homologation of methanol to ethanol [16]. Ethanol was formed under forced reaction conditions from CO + H_2 mixtures (200 atm, 200-250°C) in methoxy-terminated polyglycol solvents like diglyme, $(MeOCH_2CH_2)_2O$, in the presence of cobalt carbonyl catalysts. Experiments with ^{13}CO showed >90% of the ethanol to derive from the methyl groups of the solvent and only about 5% from pure syn gas chemistry. Acid catalyzed scission of the solvent by the relatively strong acid $HCo(CO)_4$ may initiate the reaction by forming a methyl cobalt species [17]. The products derived from synthesis gas by Co or Rh carbonyl homogeneous catalysts are concluded to be formed via formaldehyde as the key intermediate. The ratio of the two group of products, i.e. those derived from methanol and from ethylene glycol is determined by the direction of addition of the metal hydride to the C=O bond to yield either a hydroxymethyl-cobalt (1) or a methoxy-cobalt (2) intermediate [18]:



The hydrogenation of CO at 230°C and 200 atm was investigated with $Co_2(CO)_8$ catalyst in toluene solution and $Ru_3(CO)_{12}$ in N-methylpyrrolidone solution. The latter system gave almost exclusively C_1 compounds (MeOH and HCOOMe). The Co catalyst furnished also ethyleneglycol; its yield increased with pressure and Co concentration [19].

Ethylene glycol acetate is formed from synthesis gas in glacial acetic acid solutions of Ru(III) salts, e.g. $RuCl_3.xH_2O$, in combination with large cationic species such as quaternary phosphonium salts, as catalyst precursors [20]:

$$2\ CO + 3\ H_2 + 2\ HOAc \longrightarrow (CH_2OAc)_2 + 2\ H_2O$$

RuO_2 dispersed in a molten quaternary phosphonium or ammonium salt (e.g. Bu_4PBr) is a catalyst system for the direct synthesis of ethylene glycol (with methanol and ethanol as byproducts) from CO and H_2 [21]. With both systems reaction conditions are 220°C and 430 atm CO + H_2 pressure, and catalysis presumably involves anionic ruthenium carbonyl species like $HRu_3(CO)_{11}^-$. Hydrogenation of CO at 260° and 640 atm over $Ru_3(CO)_{12}$ catalyst in carboxylic acids gave MeOH and small amounts of glycol esters. Other polar solvents as EtOH or EtOAc gave only MeOH [22]. Ionic iodide promoters (e.g. KI) enhance the activity of Ru complexes for CO hydrogenation and simultaneously increase their selectivity to two-carbon products, especially ethylene glycol and ethanol. The ethanol is largely a secondary product formed from methanol. Reaction solutions contain Ru mainly in the form of $HRu_3(CO)_{11}^-$ and $Ru(CO)_3I_3^-$. Neither of these is significantly active alone, even in the presence of iodide promoters. However, mixtures of the two complexes, possess catalytic activity [23].

A ^{14}C labeling study showed that $>90\%$ of CO reduced to MeOH by V(II)-catechol complexes in alkalic MeOH proceeds without intermediate formation of free formaldehyde. A mechanism is proposed which permits both a direct 4 electron reduction to MeOH and a 2-step 2 electron process with CH_2O intermediate [24].

3. Hydroformylation

a) Co Catalysts

$Co_2(CO)_8$ or cobalt acetate + PBu_3 catalysts are inactive for the hydroformylation of propene at 85°C and 80 atm. However, a highly selective reaction ($>99\%$ n-butanal) sets in if the reaction mixture is irradiated with a high pressure mercury lamp and methanol is used as a solvent (no reaction in hydrocarbons). The effect of irradiation is less pronounced in the absence of phosphine: with $Co_2(CO)_8$ as catalyst no change in reaction rate is observed, if cobalt acetate is used, light is only needed to start the catalytic reaction. With higher olefins, hydrogenation is observed as a side reaction [25]. The $Co_2(CO)_8$ and $Co_4(CO)_{12}$ catalyzed hydroformylation of octene-1 and cyclohexene in hydrocarbon solvents is strongly retarded by UV irradiation. Apparently 17-electron species of the type $\cdot Co(CO)_3L$ (L = CO or PBu_3) produced by the photolytic cleavage of the corresponding dimers, are not able to activate H_2 [26]. In MeOH as solvent, however, the hydroformylation of cyclohexene with $Co_2(CO)_8$ is enhanced by UV irradiation, probably via activation of the $Co(CO)_4^-$ anion.

The $[Co(CO)_3(PBu_3)_2][Co(CO)_4]$ complex is photochemically converted to $HCo(CO)_3(PBu_3)$, a very selective catalyst for the formation of n-aldehydes from α-olefins [27].

$Co_2(CO)_8$ + diphosphine catalysts are effective for the hydroformylation of allyl acetate and allyl formate; the activity decreases in the order: diphos $>$ cis-$Ph_2PCH{=}CHPPh_2$ $>$ $Ph_2PC{\equiv}CPPh_2$ $>$ none $>$ $Ph_2PCH_2PPh_2$ $>$ PPh_3 [28].

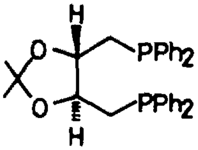
Bisolefinic carbamates and N,N-diallyl N-substituted amines have been subjected to hydroformylation with $HCo(CO)_4$, $Co_2(CO)_8$ and $HRh(CO)(PPh_3)_3$ as catalysts. The products differ with amines and carbamates and the catalysts, but the expected formation of medium-sized heterocyclic rings has not been observed [29]. NCCHMeCOOMe, $NCCH_2CH_2COOMe$ and $NCCHMeCOOCHMe_2$ were isolated and identified by their mass spectra among the products of the hydroformylation of acrylonitrile in MeOH [30]. In the hydroformylation of C_{11} olefins the optimum alcohol yield was obtained at 230° using 1 $Co_2(CO)_8$ + 1.2 $Fe(CO)_5$ + 10.2 N-methylpropyrrolidine [31].

b) Rh Catalysts

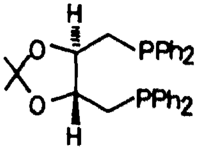
Square planar $Rh(CO)_2LCl$ (L is N-bonded $o\text{-}H_2NC_6H_4CO_2H$) shows good catalytic activity in propene hydroformylation in the presence of PPh_3 [32]. Several Rh complexes were found to be catalysts for the hydroformylation of heptene-1 at 100°C: Rh(COD)(tropolonate) in the presence of excess PPh_3 [33], $(Rh(NBD)[P(C_6H_4R\text{-}p)_3]_2)(ClO_4)$ complexes (R = MeO, Me, F, Cl) [33a], $[Rh(COD)_2](ClO_4)$ and $[Rh(COD)_n(stilbenediamine)](ClO_4)$ (n = 1 or 2) [34].

Using $Rh(CO)(PPh_{3-x})(N\!<)_x]_2Cl$ complexes as catalysts for hydroformylation of hexane-1 indicated that the ratio normal/branched aldehyde increases with increasing π-acceptor property of the ligand [35]. In the presence of $Rh(CO)(PAr_3)_2Cl$ catalysts (Ar = Ph, $p\text{-}EtC_6H_4$, $p\text{-}BuC_6H_4$ and $p\text{-}C_5H_{11}C_6H_4$) the n/i ratio is enhanced by the presence of p-alkyl substituents on the phenyl groups of triphenylphosphine. The rate of reaction is, however, decreased by increasing chain length and the optimum compromise is obtained when n-butyl substituents are present [36].

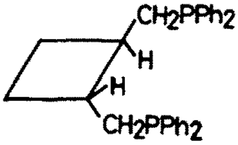
The effect of the 1,4-diphenylphosphinobutanes (+)-DIOP (3a), (4), (5) and (6), which differ in rigidity around the 2,3 C-C bond, on the hydroformylation of 1-hexene catalyzed by $HRh(CO)(PPh_3)_3$ has been investigated. At stoichiometric or higher ratios ($P\frown P$:Rh $>$ 1.5:1) DIOP and (4) conferred higher (up to 87%) while (5) and (6) lower selectivities to the linear aldehyde. High selectivities to linear aldehyde may also be obtained by 1:1 molar combinations of diphosphine and $HRh(CO)(PPh_3)_3$ if a suitable monophosphine is added.



3a
(+)-DIOP



3b
(-)-DIOP



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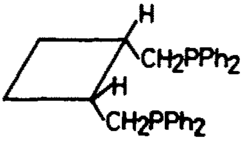

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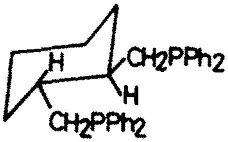

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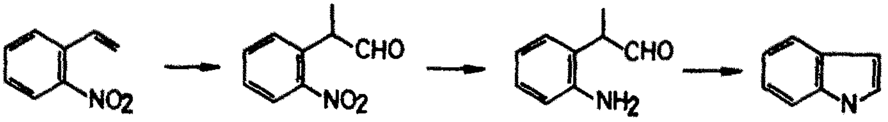
The hydroformylation of hexene-1 with $HRh(CO)(PPh_3)_3$ as catalyst was studied using different experimental techniques. Without solvent the ratio of n- to iso-aldehyde increased as the PPh_3 concentration increased, as the total pressure decreased and as the temperature increased until it peaked at 90° [38]. If the catalyst was dissolved in molten PPh_3 a high ratio of straight chain versus branched chain aldehydes was found. Lowering the temperature and pressure increased this ratio and decreased the isomerization of 1-hexene to 2-hexene [39]. The supported liquid phase (SLP) method has been also employed [40]. Apparently gas--phase reactions with supported liquid-phase catalysts (SLPC) are not limited to reactants which give only low-boiling products.

Several p-substituted styrenes were hydroformylated with $HRh(PPh_3)_4$ as catalyst. The selectivity for α-aldehyde formation increased with the σ_p value of the substituent. In competitive hydroformylation of p-substituted styrenes and styrene the relative rate increased with the σ_p values [41].

Hydroformylation of $CH_2=CRCH_2CH(OEt)_2$ (R = (S)-EtCHMe) at 80-100° under 100 atm 1:1 $CO:H_2$ in the presence of $Rh(CO)(PPh_3)_2Cl$ gave 65-75% $OCHCH_2CHRCH_2CO(OEt)_2$ [42]. Under hydroformylation conditions (160°C, 160 atm $CO:H_2$ = 1:1) using supported Rh catalysts such as Rh/Al_2O_3 and Rh/C, 2-nitrostyrene is directly converted into skatole (7) in ca. 70% yield:



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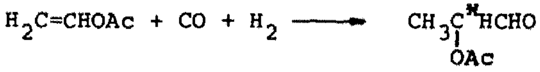
2-Aminoacetophenone is formed as a byproduct [43].

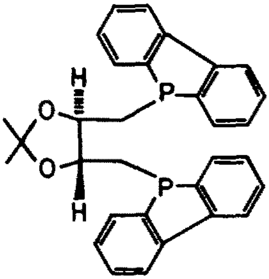
Rh catalysts containing phosphine ligands with surfactant structure can be used for hydrogenation or hydroformylation of olefins in a two phase liquid system. After reaction the oily phase containing the product is removed, while the aqueous phase containing the catalyst is ready for a new reaction [44]. The preferential hydrogenation and hydroformylation of 9-decen-1-ol in presence of 10-undecen-1-ol has been achieved in an aqueous bilayer dispersion of dipalmitoylphosphatidylcholine with the water soluble catalyst $HRh(CO)(dpm)_3$ [45].

The asymmetric hydroformylation of vinyl acetate



$$H_2C{=}CHOAc + CO + H_2 \longrightarrow CH_3\underset{\displaystyle OAc}{\overset{*}{C}}HCHO$$

and related esters was carried out in the presence of Rh complexes and chiral phosphine ligands of the DIOP type at 60-100°C, 10-70 atm in benzene as solvent. Ligand structure and the ligand/metal ratio were the primary factors controlling asymmetric induction. The highest induction efficiencies (up to 51%) were obtained with (-)-DIPHOL (8). This is the highest optical yield reported for hydroformylation until now [46].



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c) Pt Catalysts

The complexes $Pt(CO)(ER_3)Cl_2$ (E = P, As; R = aryl, alkyl) are active catalyst precursors for the hydroformylation of olefins in the presence of added $SnCl_2$. Terminal aliphatic monoolefins are hydroformylated readily with a high n/i aldehyde ratio. Little competing olefin hydrogenation was observed under conditions favourable for maximum hydroformylation [47]. The hydroformylation of 1-alkenes is efficiently catalyzed by $PtCl_2$ + diphosphine + $SnCl_2$ catalysts if the diphosphine is a 1,4-bis(diphenylphosphino)butane derivative with a rigid ring skeleton like DIOP. Reaction rates were higher than when using $HRh(CO)(PPh_3)_3$ and up to 99% linear aldehydes were obtained [48].

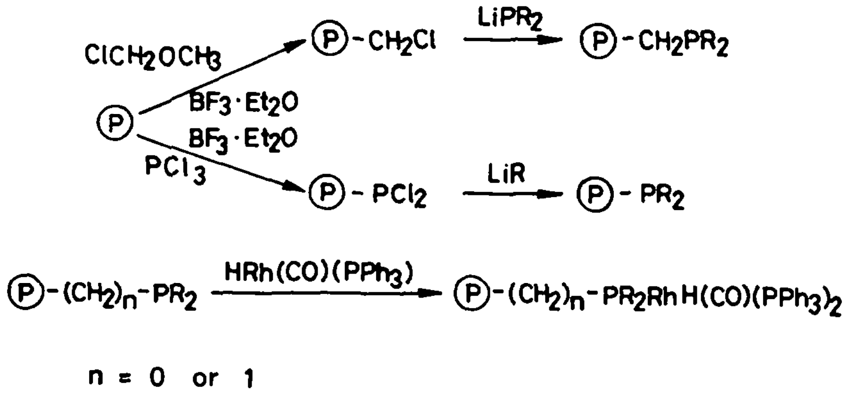
d) Other Metals

The hydroformylation of 1-octene catalyzed by $M(C_5R_5)(CO)_2X$ and $M_2(C_5R_5)_2(CO)_4$ species (R = H, Me, Ph; M = Fe, Ru; X = Cl, Br, I) has been examined at 135°C under 85 atm ($CO + H_2$). The reaction rates were generally low for all reactions observed (hydroformylation, olefin isomerization and hydrogenation, aldehyde hydrogenation). The results support $HFe(C_5R_5)(CO)_2$ as the single catalytically active species in the case of iron whereas in the case of ruthenium the monomeric hydride $HRu(C_5R_5)(CO)_2$ is responsible for hydroformylation but the dimeric $Ru_2(C_5R_5)_2(CO)_4$ may account for a large part of olefin isomerization. The activity of the complexes decreased with substitution of the cyclopentadienyl ring (R = H $\gg$ Me, Ph). The Ru complexes were in most cases more active than the Fe analogues [49].

e) Heterogeneous Systems (Supported Complexes)

Supported liquid phase catalysts (SLPC) were prepared from $HRh(CO)(PPh_3)_3$ and PPh_3 (or $P(p\text{-}tol)_3$) on different silica supports for the gas phase hydroformylation of allyl alcohol at 88-108°C and 1.2-4 atm. Very high selectivities (up to 99%) for 4-hydroxybutyraldehyde were obtained. The side reaction to propionaldehyde can be suppressed by using a silica with low aluminium content. No sign of deactivation was observed after 250 hours [50]. 1-Heptene has been hydroformylated in the gas phase at 120°C and 3-9 atm with a solution of $HRh(CO)(PPh_3)_3$ in molten PPh_3 adsorbed in the pores of the carrier Chromosorb. The ratio of n/i aldehyde is higher (46/1) than in liquid bulk hydroformylation [51]. Supported liquid phase catalysts composed of $HRh(CO)(PPh_3)_3$ and PPh_3 supported on silica have been used for the hydroformylation of propene. Additional solvents like biphenyl, tetraethyleneglycol, etc. increase the reaction rate but decrease the regioselectivity for n-butanal production. The kinetics of the reaction has been determined [52].

Catalysts have been developed by anchoring $HRh(CO)(PPh_3)_3$ to the surface of macroreticular polystyrene - divinylbenzene by one of the following methods:



Unpolymerized vinyl groups may also take part in these functionalizations. The original support texture is not affected during the catalyst preparation [53]. These catalysts have high activity per g of Rh for the heterogeneous gas phase hydroformylation of propylene at 90°C and 1 atm. Additional PPh_3 improves the activity as well as the selectivity [54]. Hydroformylation catalysts were also prepared by direct impregnation of either silica or alumina by benzene solutions of $HRh(CO)(PPh_3)_3$.The complex becomes so strongly bound that subsequent washing with boiling benzene does not lead to loss of Rh, phosphine or catalytic activity. It is assumed that the active hydroformylation centres are formed by a support-induced rearrangement of the bound complex accompanied by the dissociation of PPh_3 analogous to a solvent-assisted dissociation [55].

1-Hexene was hydroformylated in the presence of cobalt carbonyl supported on 4-vinylpyridine grafted onto polypropylene. The ratio of normal/branched heptanal formed was by a factor of about 2.5 over that obtained with the corresponding homogeneous catalyst [56].

Polymer-bound Ru catalysts were prepared by reacting diphenylphosphinated styrene + 1% divinylbenzene resins with $Ru(CO)_3(PPh_3)_2$ under CO. These resins functioned as 1-pentene hydroformylation catalysts without olefin isomerization and some of them gave high (3.5-3.8) normal/branched aldehyde selectivities [57].

1-Pentene has been hydroformylated with $RhCl_3 \cdot 3H_2O$ as a catalyst at 150°C and 40 atm CO + H_2 (1:1) in the presence of Sirotherm (a thermally regenerable ion-exchange resin used for desalination). Rate measurements indicate that at higher temperatures a larger fraction of Rh is released from the resin and acts as a homogeneous catalyst. Upon cooling, efficient uptake of Rh from the solution was observed [58].

4. Homologation of Alcohols, Ethers, Esters and Carboxylic Acids with CO + H_2

The methanol homologation reaction

$$CH_3OH + CO + 2\ H_2 \longrightarrow CH_3CH_2OH + H_2O$$

catalyzed by cobalt carbonyls and iodine as a promoter has been modified by adding α,ω-bis(diphenylphosphino)alkanes $[Ph_2P(CH_2)_nPPh_2,\ n = 1\text{-}6]$ as ligands. Ethanol selectivity as high as 89% was achieved by using the n = 6 bisphosphine at 200°C and 180 atm (H_2:CO = 2:1). At 150°C acetaldehyde was the main product

[59]. Salts of the $FeCo_3(CO)_{12}^-$ anion promoted with MeI were found to be superior to other cobalt + iodine homologation catalysts. Mixtures of $Fe(CO)_5$ and $Co_2(CO)_8$ in the presence of Bu_4NI gave identical results. The nature of the active catalyst species is not known [60]. The mixed-metal clusters $PdCo_2(CO)_7$(diphos) and $X[RuCo_3(CO)_{12}]$ (X = Na, Cs, Et_4N) show improved catalytic activities for the homologation of methanol as compared to $Co_2(CO)_8$ at 180°C and 120 atm (H_2:CO = 2:1). The best result (51% selectivity to ethanol) was achieved with $(Et_4N)[RuCo_3(CO)_{12}]$ [61].

Homologation of methyl formate to ethyl formate or ethanol

$$HCOOCH_3 + CO + 2H_2 \longrightarrow HCOOC_2H_5 + H_2O$$

$$HCOOCH_3 + CO + H_2 \longrightarrow C_2H_5OH + CO_2$$

is catalyzed by Ru compounds in the presence of MeI at 220°C and 270 atm (CO:H_2 = 1:1). Tertiary phosphines promote the reaction but gradually deteriorate under the severe reaction conditions, mainly by quaternization. Reaction rates and yields of C_2 compounds are low [62]. The simultaneous carbonylation and homologation of dimethyl ether to ethyl acetate with CO and H_2 using Ru catalysts in conjunction with iodide promoters and an acid (CH_3COOH, HI) was studied at 200° and 100-300 atm. The highest selectivity was about 70%. The catalytically active species is apparently an anionic iodocarbonyl Ru derivative $Ru(CO)_xI_y^-$ which reacts with the protonated substrate to give a MeRu species [63].

The direct homologation of aliphatic carboxylic acids

$$RCOOH + CO + 2H_2 \longrightarrow RCH_2COOH + H_2O$$

has been achieved in the presence of soluble ruthenium species e.g. RuO_2, $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, coupled with iodide-containing promoters such as HI or an alkyl iodide. Reaction conditions are 220°C and 270 atm initial pressure (CO:H_2 = 1:1), total selectivity for homologous acid formation is about 45%. $Ru(CO)_3I_3^-$ is the main species present in the solution under reaction conditions [64-67].

5. Coordination Chemistry Related to CO Hydrogenation and Hydroformylation

The cluster $Co_3(CO)_9COH$ has been proposed as an intermediate of the hydrogenation of CO in homogeneous phase by cobalt carbonyls as catalysts [68]. Its methyl derivative $Co_3(CO)_9COMe$ reacts with CO + H_2 (115 atm, 120°C)in the presence of $Co_2(CO)_8$ to form MeOMe, $MeOCH_2CH_2OH$ and $MeOCH_2CH_2OCHO$ suggesting such trinuclear derivatives as possible intermediates for the formation of glycol from synthesis gas too. $Co_3(CO)_9CR$ (R = H, D, nBu) complexes react at 100-120°C with synthesis gas (90-120 atm) to give RCHO, $Co_2(CO)_8$ and $HCo(CO)_4$. This reaction has been discussed as part of an alternative mechanism for the hydroformylation reaction [69]. The triethylamine adduct $Co_3(CO)_9COH.Et_3N$ is formed from $HCo(CO)_4$ and $Co_2(CO)_8$ in the presence of Et_3N at 10°C in vacuum; in the absence of Et_3N, $Co_3(CO)_9H$ is formed under such conditions, presumably over $Co_3(CO)_9COH$ [70].

Metal-formyl complexes are considered as probable intermediates in the metal catalyzed reduction of CO by H_2. There is now the first report of a metal-formyl complex which forms from the reaction of a metal hydride with CO. Rhodium octaethylporphyrin hydride reacts with CO to form a neutral metallo-formyl complex [71]:

$$\mathrm{Rh(OEP)H + CO \longrightarrow Rh(OEP)CHO}$$

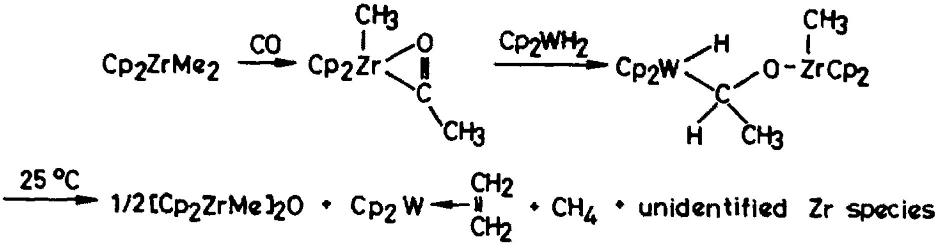
High pressure IR studies suggest, that $Rh_{17}(CO)_{32}(S)_2^{8-}$ maintains its structural integrity under the reaction conditions used for the conversion a synthesis gas to alcohols and apparently acts as the catalyst [72].

The stepwise reduction of CO to CH_4 on a Os_3 cluster face was realized by the following transformations [72a]:

$$\mathrm{Os_3(CO)_{12} + BH(O\text{-}Pr^i)_3^- \xrightarrow[0^o]{THF} Os_3(CO)_{11}(CHO)^-}$$

$$\mathrm{\xrightarrow{H_3PO_4} Os_3(CO)_{11}CH_2 \xrightarrow[70-80]{H_2(D_2)} CH_4\ (CH_2D_2)}$$

In the reaction of CO with Cp_2TiCl_2 + $AlMe_2Cl$, Ti(IV) was reduced to Ti(II) and CO was converted to CH_2O and ketene. A kinetic study of the reaction was reported [73]. The stoichiometric synthesis of ethylene incorporating carbon from CO has been described [74]:

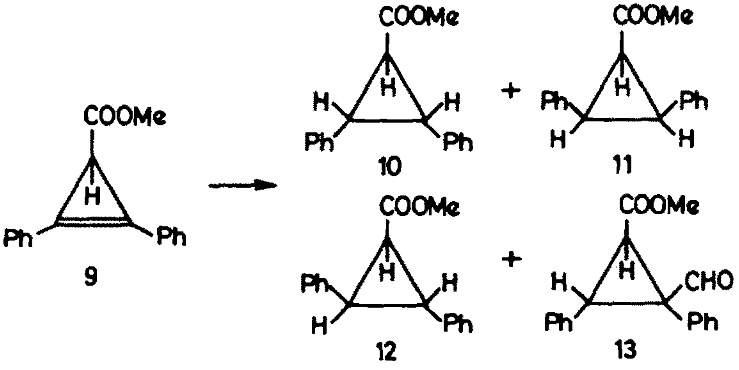


Hydrogenation of equimolar mixtures of $LiNMe_2$ and different metal carbonyls [$Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Fe(CO)_5$] in HMPA at 130°C and 2.4 atm H_2 results in the formation of small amounts of DMF and Me_3N. Me_3N arises from reduction of the primary product DMF, the active hydrogenation agent is the $HCr(CO)_5^-$ anion [75].

The reaction of $HCo(CO)_4$ with olefins and CO to form acylcobalt tetracarbonyls:

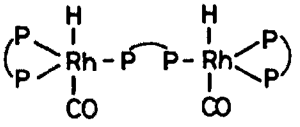
$$RCH{=}CH_2 + HCo(CO)_4 + CO \longrightarrow RC_2H_4COCo(CO)_4$$

is a component of the hydroformylation catalytic cycle. It has been shown that in the case of linear α-olefins the reaction is catalyzed by $Co_2(CO)_8$, presumably by generating radical species like $\cdot Co(CO)_4$ [76]. Reaction of $HCo(CO)_4$ with the diphenylcylopropene (9) leads to the three possible hydrogenated cyclopropanes (10-12) but to only one of the four possible aldehyde isomers (13):



The formation of (13) as the exclusive hydroformylation product is consistent with a concerted cis addition of $HCo(CO)_4$ to the more hindered face of (9) [77].

The ^{31}P NMR spectra of Rh complexes that form in solution via ligand exchange of diphosphines with $HRh(CO)(PPh_3)_3$ have been scanned in order to characterize these complexes. With certain diphosphines such solutions catalyze hydroformylation and have high selectivity for linear aldehyde formation. The results support the conclusion that complexes with high selectivity for n-aldehydes have 3 phosphine ligands coordinated to Rh at the instant that selectivity is determined (see 14 and 15) [78], cf. [37].



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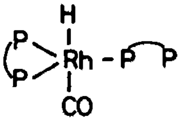

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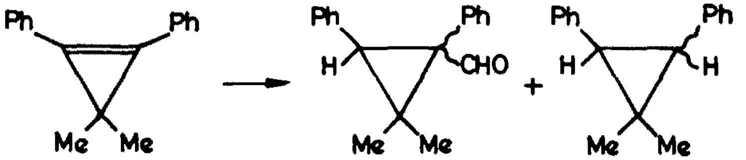
Infrared spectral evidence has been obtained at 5-12°C and 1542 atm ($CO:H_2$ = 4.5:1) for the existence of $HRh(CO)_4$, a complex often proposed as the active species in reactions of CO and H_2 in the presence of rhodium carbonyls as catalysts [79].

1,1-Diphenyl-3,3-dimethylcyclopropene (16) reacts with $HMn(CO)_5$ at 55°C to give the aldehydes (17) as hydroformylation products and the cyclopropanes (18) as hydrogenation products:

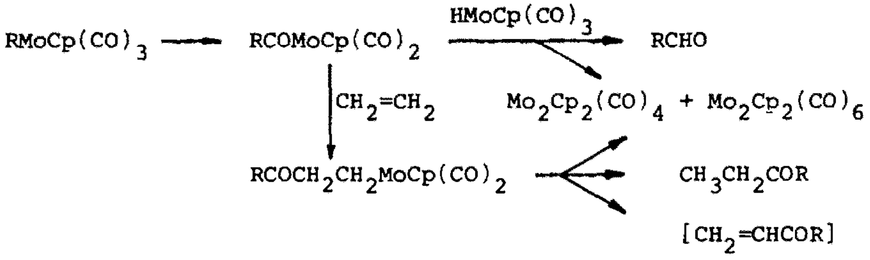


16 17 18

cis : trans = 87 : 13 cis : trans = 87 : 13

The lack of stereospecificity and the observed CIDNP effect supports a radical intermediate. This is the first example for a stoichiometric hydroformylation with $HMn(CO)_5$ [80].

The complexes $RMoCp(CO)_3$ (R = Me, Et) react with ethylene at 100^{o} and with $HMoCp(CO)_3$ at 25-50^{o} to yield ketones and aldehydes:



These reactions model some essential steps of the catalytic hydroformylation reaction [81].

6. Water Gas Shift Reaction

The water gas shift reaction

$$CO + H_2O \longrightarrow CO_2 + H_2$$

is catalyzed by several transition metal complexes. Rh(I)-hydrido compounds e.g. $HRh(PPr_3)_3$ as catalyst precursors are active under relatively mild conditions (50^{o}C) in pyridine or acetone solutions without further additives. Several catalytic cycles operate in this system, all involving [trans-$Rh(CO)L_2(solv)$]OH (L = tertiary phosphine like PPr_3) as the key intermediate. Many other rhodium species were isolated from the reaction mixture and the elementary steps of the catalytic cycles studied independently [82].

The hexacarbonyls of Cr, Mo and W in basic MeOH + H_2O solutions at$<200^{o}$C provide turnover numbers up to 12000 mol H_2/mol of $M(CO)_6$ per day. The key steps of the mechanism proposed are the reaction of the formate ion with $M(CO)_5$ and the decomposition of the formato anion $M(CO)_5HCO_2^-$ to produce CO_2 and H_2 in the presence of H_2O [83].

$RuCl_3$ in a KOH/H_2O solution catalyzes the water gas shift reaction at 90^{o}C and near atmospheric pressure. This catalyst is more active than the $Ru_3(CO)_{12}$ + KOH system previously described [84]. $Ir(COD)L_2^+$ complexes (L or L_2 = mono or bidentate ligands with

P and N as donor atoms) are also active catalysts [85]. $Os_3(CO)_{12}$ supported on acid zeolite reacts at 180-240° with hydroxyl groups of the support to give catalysts for the water gas shift reaction performed at 140°. The catalytic activity depends on the thermal treatment [86].

7. Reductions with $CO + H_2O$

Acetone is catalytically reduced to iPrOH by CO and H_2O in the presence of iron carbonyls and Et_3N at 100°C and 100 atm:

$$Me_2CO + CO + H_2O \longrightarrow Me_2CHOH + CO_2$$

The $Et_3NH{\cdot}HFe(CO)_4$ system effects the reduction of n-butyraldehyde to nBuOH at room temperature in a stoichiometric reaction. The Et_3NH^+ cation is apparently necessary for the transfer of a H^+ to the carbonyl group [87]. Kinetics and mechanism of reduction of benzaldehyde with CO and H_2O using $Rh_6(CO)_{16}$, $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$ as catalysts were studied. Results with substituted benzaldehydes indicate that the aldehyde is involved in the rate-determining step [88].

The Ru(II) complexes $[Ru(COD)py_4](BPh_4)_2$ and $Ru(CO)_2py_2Cl_2$ are active catalysts for the reduction of nitrobenzene to aniline by CO in H_2O/THF solution at 80-145°C and 50-80 atm:

$$PhNO_2 + 3\ CO + H_2O \longrightarrow PhNH_2 + 3\ CO_2$$

Water is essential for the reaction but no base needs to be added [89]. With $Rh_6(CO)_{16}$ as catalyst the reaction proceeds already at 1 atm but an amine is necessary. The activity of the catalyst depends strongly on the structure of the amine, γ-aminopyridines were found to be the most favourable [90].

8. Reaction of Olefins with $CO + H_2O$

Complexes prepared in situ from $Co_2(CO)_8$ and diphos are active catalysts for the hydroformylation of propylene with CO and H_2O at 160° and 100 atm. Butyl alcohols, butyric acids and dipropylketones are formed as byproducts. Increasing the temperature leads to more alcohol, the catalyst solutions reduce PrCHO to BuOH. If propene is present in excess, predominantly ketones are formed [91, 92]. The hydrocarbonylation of ethylene with CO and H_2O catalyzed by $Co_2(CO)_8$ + diphos produces Et_2CO with 99 ± 1% selectivity. The active species which catalyze the water gas shift reaction participate also in the hydrocarbonylation of ethylene [93].

α-Olefins are hydroformylated to the corresponding aldehydes and alcohols by CO + H_2O with a $Rh_6(CO)_{16}$ + amine catalyst system at 80°C and 5 atm. $Me_2N(CH_2)_3NMe_2$ and 4-dimethylamino pyridine favour the formation to alcohols, less basic monoamines (like py) yield mainly aldehydes and olefin isomers. Triethylamine is not a good additive. α,β-Unsaturated carbonyl compounds are hydrogenated to saturated carbonyl compounds [94]. No basic additives are needed with $H_2Rh(PPr_3)_2(O_2COH)$ as catalyst [95]. Olefins with electron withdrawing groups like methyl crotonate are mainly hydrogenated. However, simple aliphatic olefins, styrene and derivatives give mainly hydroformylation products. The catalyst is less efficient for the hydrogenation of >CO, $-NO_2$ and -CN groups.

III. Hydrogenation and Reduction

1. H-D Exchange

Photolysis of C_6D_6 solutions of p-xylene, Me_2O, etc. in the presence of $H_3MoCp(Me_2PCH_2CH_2PMe_2)$ causes the statistical exchange of all or many of the H atoms with D. The hydrogens of the coordinated ligands of the Mo complex and also those of other organometallic compounds are similarly exchanged [96]. Pt(II) σ-aryl complexes are intermediates in the Pt(II) catalyzed H-D exchange of aromatic hydrocarbons [97].

Aqueous solutions of H_2O_2 and reducing metal ions like Fe^{2+} (Fenton's reagent), Ti^{3+}, V^{3+} and Cr^{2+} effect a small amount of H(T)-exchange with dissolved dioxane or diethyl ether. The metal ions are thought to act by reducing the organic radicals to metal-organic intermediates which decompose with aqueous H^+ [98]:

$$M^{n+} + R^{\bullet} \longrightarrow (M-R)^{n+} \xrightarrow{H^+} M^{(n+1)+} + RH$$

$Ru_3(CO)_{12}$ catalyzes at 150°C and 28 atm the D for H exchange of tertiary amines (Et_3N, Pr_3N and Bu_3N) where D_2O serves as a source of D. The exchange site selectivities (α vs. β) correspond closely to those found for Pd black [99].

2. Hydrogenation of Olefins

a Fe, Ru and Os Catalysts

A Et_3Al + $FeSt_3$ catalyst (Al:Fe = 5:1) was used for hydrogenation of sunflower oil [99a]. Hydrogenation, hydrosilylation and isomerization of 1-pentene in the presence of $Fe(CO)_5$ and $Fe_3(CO)_{12}$ has been studied under photocatalytic conditions using very high light intensity excitation to make the catalyst turnover rate (and not the photogeneration of the catalyst) the rate-limiting feature. Turnover rates (olefin/catalyst.min) up to 3700 and turnover numbers (mol product/mol Fe) up to 400 were observed. The active species are supposed to be unsaturated ground-state species [100].

The catalytic activity of $Ru_3(CO)_{12}$ solutions for the isomerization and hydrogenation of 1-hexene has been compared with that prepared by impregnating silica with $Ru_3(CO)_{12}$ and heating it at 100°C under vacuum. The behaviour of the supported carbonyl complex resembles that of a heterogeneous catalyst (prepared by heating it to 200°C in vacuum) more than that of the soluble carbonyl cluster [101]. Ru(II) and Rh(I) complexes with alternating copolymers of maleic acid and different vinyl ethers have been prepared starting from $H_2Ru(CO)(PPh_3)_3$ and $HRh(CO)(PPh_3)_3$. In addition $Ru(PPh_3)_3Cl_2$ was used to obtain heterogenized complexes through reaction with the Na salts of poly(acrylic acid) and ethylene/maleic acid copolymer. The carboxylic groups function as ligands for anchoring the metal complexes. The complexes were tested as catalysts for the hydrogenation and isomerization of 1-pentene [102]. $Ru(PPh_3)_3Cl_2$ has been attached to phosphinated polystyrene crosslinked with 2% divinylbenzene and converted in the presence of base to the polymer supported analogue of $HRu(PPh_3)_3Cl$. This catalyst hydrogenates terminal olefins under ambient conditions. At low loadings of Ru on polymer the rates approach those corresponding to the homogeneous system [103].

The Ru(II) complexes $Ru(AsPh_3)_3Cl_2$, $Ru(SbPh_3)_3Cl_2$, $Ru(DMSO)_4Cl_2$, $Ru(SbPh_3)_3(DMSO)Cl_2$, $Ru(diphos)_2Cl_2$, $Ru(Ph_2AsCH_2CH_2AsPh_2)_2Cl_2$ were used as catalysts in the homogeneous hydrogenation of cyclohexene at 30° and 1 atm H_2 [104].

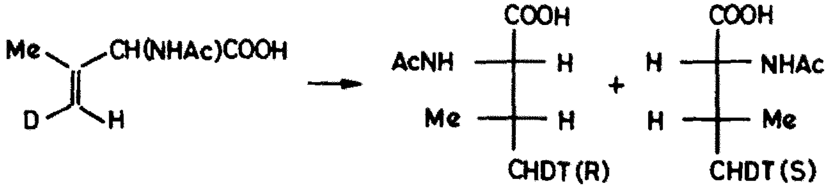
In ethylene hydrogenation at 75-110°C the anchored metal clusters $H_2Os_3(CO)_9(PPh_2CH_2CH_2\text{-}SG)$ and $Os_3(CO)_{11}(PPh_2CH_2CH_2\text{-}SG)$ give lower rates than their homogeneous counterparts (H in place of SG). At 150°C $Ru_6C(CO)_{16}(PPh_2CH_2CH_2\text{-}SG)$, $Rh_2(CO)_4(SG)$ and $Rh(CO)_2(PPh_2CH_2CH_2\text{-}SG)$ give active hydrogenation catalysts, but supported metals appear to form under the reaction conditions [105].

b) Co, Rh and Ir Catalysts

The complexes $RCo(CO)_2[P(OMe)_3]_2$ (R = Me, Ac) catalyze the hydrogenation of terminal olefins at ambient conditions. Several related complexes, including the hydride (R = H), are inactive as catalysts. The proposed mechanism involves a series of methyl → acetyl interconversions which open the necessary sites for the coordination of olefin and H_2 [106].

Allyl alcohol is hydrogenated and isomerized to PrOH and EtCHO, respectively, by H_2 in the presence of Na[Rh(HL)Cl] (H_4L = EDTA) and $NaBH_4$ [107].

The H_2 pressure significantly influences the ratio of cis/trans isomers in the hydrogenation of 4-tert-butylmethylenecyclohexane in the presence of $HRh(PPh_3)_4$ [108]. Hydrogenation of (2R,S)-(E)-(4-D)-N-acetylisodehydrovaline (19) with HT and $Rh(PPh_3)_3Cl$ as catalyst gave preferentially (≈95%) a mixture of (2S,3S,4R)-(4-DT)-N-acetylvaline (20) and its enantiomer (21):



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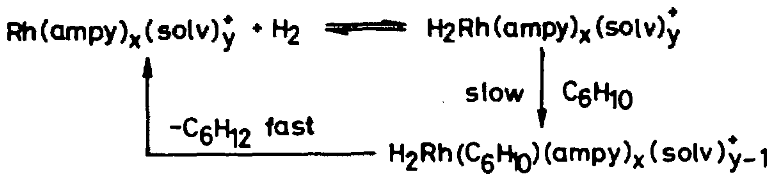
Accordingly catalytic hydrogenation with $Rh(PPh_3)_3Cl$ occurs with preference for 3-re, 4-si attack on the S-component and 3-si, 4-re attack on the R-component [109]. The kinetics of homogeneous hydrogenation of cyclohexene in EtOH in the presence of the catalytic system $Rh_2(C_8H_{14})_4Cl_2$ + 2-aminopyridine (ampy) has been investigated (C_8H_{14} = cyclooctene). The results support the following catalytic cycle:



The catalyst is about 10 times more active than $Rh(PPh_3)_3Cl$ [110].

Reaction of the unstable $(Me_4N)(C_2B_{10}H_{13})$ with $Rh(PPh_3)_3Cl$ produced closo-1,1-$(PPh_3)_2$-1-H-1,2,4-$RhC_2B_{10}H_{12}$ which catalytically hydrogenates blocked olefins under mild conditions [111]. The reaction of $Rh(PPh_3)_3Cl$ and Cs[7,8-bis(butenyl)-7,8-$C_2B_9H_{10}$] yields [closo-1,3-μ-2,3-μ-(1,2-μ-(η^2-3,4-$CH_2CH_2C(Me)=CHCH_2CH_2CH_2$))-3-H-3-$PPh_3$-3,1,2-$RhC_2B_9H_9$] which catalyzes the hydrogenation and isomerization of alkenes at 25°C in THF solution. The complex may be recovered unchanged from these solutions [112].

Ag(I) polystyrene sulfonate absorbs tertiary phosphines from organic solutions and restores PPh_3-inhibited homogeneous hydrogenation of alkenes by $Rh(PPh_3)_3Cl$ to a non-inhibited rate [112a]. The liquid phase hydrogenation of alkenes catalyzed by homogeneous Rh(I) complexes prepared in situ from $Rh_2(alkene)_4Cl_2$ and phosphines of the type $RPPh_2$ ($R = (CH_2)_nSi(OEt)_3$, n = 1-6 and $CH_2SiMe_{3-m}(OEt)_m$, m = 1-3) and by their heterogenized analogs anchored to silica has been found first order in alkenes. The deactivation observed in both cases is probably due to the formation of catalytically inactive dimeric complexes [113]. A supported Rh catalyst has been prepared from a phosphinated silica and $Rh_2(CO)_4Cl_2$. Treating it with H_2 leads to a structural change beginning with the elimination of the CO ligands and ending in the formation of metal particles with a large range of sizes. The catalyst was found to exhibit the highest activity in the hydrogenation of terminal olefins between these two stages [114]. Silica-supported Rh hydride complexes (some of them containing allyl and/or PMe_3 ligands) were prepared in which the Rh is covalently anchored to the support through a Rh-O bond. The complexes exhibit markedly different behaviour as olefin hydrogenation catalyst [115].

Several heterogenized olefin hydrogenation catalysts prepared by anchoring Rh-phosphine complexes to different solid supports were found unsuitable for kinetic measurements because of instabity (leaching of complex from the support or formation of Rh metal) or diffusion control. Only one specimen, $Rh(PPh_3)_3Cl$ on linear polystyrene could be used for kinetic study. In this case the mechanism of olefin hydrogenation proved to be essentially the same as in the homogeneous case [116]. Three linear polymers $(4\text{-}Ph_2PC_6H_4CHCH_2)_n$, $(4\text{-}Cy_2PC_6H_4CHCH_2)_n$ and $[4\text{-}Ph_2PC_6H_4CH(CH_3)N{=}C<]_n$ were used as supports for Rh complexes. The Rh was anchored by addition of $Rh_2(C_2H_4)_4Cl_2$ or $Rh_2(COD)_2Cl_2$. These catalysts were more stable and more active for cyclohexene hydrogenation than the homogeneous catalyst obtained from the Rh complexes and PPh_3 or PCy_2Ph. This is ascribed to a diminished tendency to dimerize [117]. The $Rh(PPh_3)_3Cl$ bound to different types of polystyrene was investigated by temperature programmed reduction with H_2. The chlorine is removed by H_2 activation and the rhodium is Rh(II) as found by XPS. Accordingly the complex formed around 100° is postulated as Ⓟ-RhH_2. The polymer-bound complexes were used as catalysts for hydrogenation and isomerization of olefins [118].

The homogeneous hydrogenation of cyclohexene and 1-heptene using the binuclear catalysts $Rh_2(TDDX)Cl_2$, $Rh_2(TDADX)Cl_2$ and $Ir_2(TDDX)Cl_2$ (TDDX = $C_6H_4[CH_2P(CH_2CH_2PPh_2)_2]_2$, TDADX = $C_6H_4[CH_2P(CH_2CH_2AsPh_2)_2]_2$ was investigated [119]. $[Ir(COD)(PCy_3)py](PF_6)$ readily hydrogenates hindered steroidal olefin groups from the α-face, without reducing ketone carbonyl groups, carbon-halogen bonds or cyclopropane rings. The catalyst has a much greater activity than $Rh(PPh_3)_3Cl$ and its solutions are stable to air [120]. A π-ethylbenzene complex is formed during hydrogenation of styrene using $[Ir(COD)(PMe_2Ph)_2](PF_6)$ as catalyst. This explains the anomalously low hydrogenation rates observed in this system. The same phenomenon may account for the failure of styrene to act as a hydrogen acceptor in the dehydrogenation of alkanes catalyzed by $H_2Ir(PPh_3)_2(OCMe_2)_2^+$ [120a].

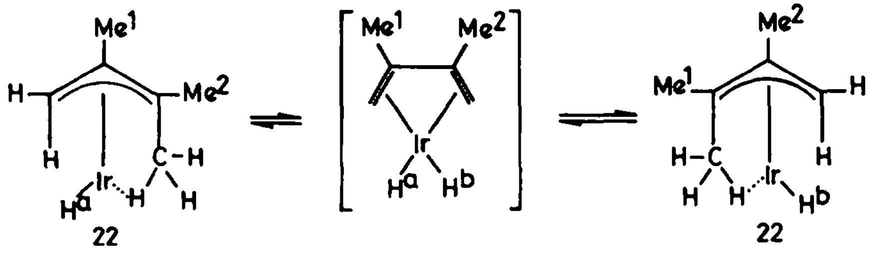
The following clusters anchored onto pendant phosphine ligands on silica surfaces have been prepared: $Ir_4(CO)_{11}[PPh_2(CH_2)_3SIL]$, $Ir_4(CO)_{10}(PPh_3)[PPh_2(CH_2)_3SIL]$ and $Ir_4(CO)_9(PPh_3)_2[PPh_2(CH_2)_3SIL]$.

These clusters are thermally stable below 330 K but do not provide catalytic activity for gas phase hydrogenation of alkenes at 300 K. The activity detected at higher temperatures seems to be due to degradation products [121]. An Ir-py complex was anchored on highly crosslinked polystyrene-divinylbenzene macroporous resins carrying phosphine groups:

$$Ir(COD)(py)_2^+ + \textcircled{P}-PR_2 \longrightarrow \textcircled{P}-PR_2Ir(COD)(py)^+ + py$$

The catalysts are highly active for the hydrogenation of 1-hexene but get more or less rapidly deactivated [122].

The first direct observation of an aliphatic C-H...M interaction and reversible hydride transfer, involving a catalytically active system has been reported. $H_2Ir(PPh_3)_2(OCMe_2)^+$ (which is an olefin isomerisation and hydrogenation catalyst) reacts with 2,3-dimethylbutadiene to give the butenyl-hydride (22). ^{31}P-NMR spectra reveal that at 258K the fluxional process shown below takes place [123]:



c) Pd Catalysts

Pd complexes with H_2salen, H_2saloph and disalicylidene-propanediamine and a Rh complex with H_2saloph catalyzed the hydrogenation of $RCH{=}C(NHAc)CO_2R^1$ ($R = R^1 = H$; $R = Ph$, $R^1 = H, Me$) [124].

When allyl alcohol is added to aqueous $[Pd(dpm)(OH)(H_2O)]_n$, H_2 is absorbed and PrOH, benzene, propylene glycol, and EtCHO are formed. Later only hydrogenation to PrOH takes place [125]. $[Pd(diphos)(Me_2CO)_2](ClO_4)_2$ catalyzes the hydrogenation of olefins at 30°C and 1 atm of H_2 in CH_2Cl_2 solution [126]. Kinetic data for cyclopentene hydrogenation on $[Pd_5(PPh)_2]_n$ catalyst in DMF indicate that a $Pd_5(PPh)_2$ + substrate complex is initially formed in a reversible step. When the catalyst concentration is increased it forms associates [127].

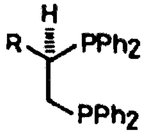
A silica-supported polyacrylonitrile-Pd(II) complex is an active and selective catalyst for alkene hydrogenation. The supported polymer catalyst also reduced $PhNO_2$ to $PhNH_2$ [128].

d) Miscellaneous

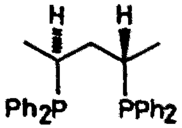
The hydrogenation of 1-hexene and cyclohexene with $LiAlH_4$ + $TiCp_2X_2$ (X = Cl, Br) catalysts was fastest at an Al:Ti ratio of 1:2 [129]. Phosphine-functionalized poly(styrene-divinylbenzene) polymers incorporating clusters with open butterfly framework structures like $AuOs_3(CO)_{10}(Ph_2P$-Ⓟ$)Cl$ and $Co_2Pt_2(CO)_8(Ph_2P$-Ⓟ$)_2$ were active catalysts for ethylene hydrogenation at 1 atm and 100°C, whereas polymers incorporating clusters with closed tetrahedral framework structures as $HAuOs_3(CO)_{10}(Ph_2P$-Ⓟ$)$ and $H_2PtOs_3(CO)_{10}(Ph_2P$-Ⓟ$)_2$ had immeasurably low activity [130]. The organoactinoids $Me_2M(Me_5C_5)$(M = U, Th) supported on alumina exhibit high catalytic activity for the hydrogenation of propylene (and the polymerization of ethylene) at 25°C. Under comparable conditions these complexes are far less active ($\approx 10^{-3}$) for hydrogenation (and practically inactive for polymerization) in solution [131].

3. Asymmetric Hydrogenation of Olefins

The chiral ditertiary bisphosphines (23) and (24) were prepared and used for the asymmetric hydrogenation of (Z)-α-acylaminoacrylic acid derivatives $R'CH{=}C(COOH)NHCOR^2$ (R' = H, Ph, substituted phenyl; R^2 = Me, Ph) in form of $[Rh(COD)(P\text{-}P)](BF_4)$ complexes as catalysts (P-P = bisphosphine). Optical yields were 84-99% [132]. Rh(I) catalysts formed by the two chiral chelating six-membered ring diphosphines skewphos (25) and chairphos (26)



R = PhCH2 (23), iPr (24)



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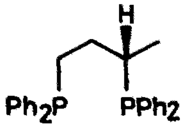

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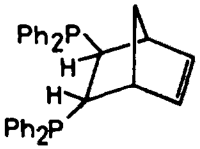
are efficient catalysts for the hydrogenation of dehydro amino acids. Skewphos generally gives high optical yields (max.98%) whereas chairphos is rather ineffective as a chiral catalyst (highest optical yield 24%). This is attributed to the difference between the conformations which the six-membered chelate rings may adopt in the catalytic intermediate: skewphos prefers a chiral skew conformation and chairphos may lead to a chair conformation which itself is achiral [133]. The ditertiary phosphines (+)-and (-)norphos (27 and 28) were used to prepare enantioselective



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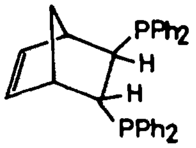

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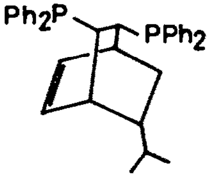
catalysts of the type $[Rh(COD)(norphos)](BF_4)$ or $Rh_2(COD)_2Cl_2$ + norphos (*in situ* catalysts) for the hydrogenation of N-acyl dehydro phenylalanine and some derivatives. Optical yields up to 97% were achieved [134, 135]. The chiral ditertiary phosphines phellanphos (29) and nopaphos (30) were prepared. Hydrogenation of prochiral olefins (31; R = H, Me, Ph; R^1 = Et, Ph, COOH; R^2 = AcNH, Ph, CH_2COOH) with $[Rh(COD)(P\text{-}P)](PF_6)$ complexes as catalyst



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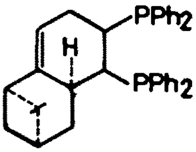
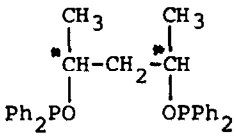


30

31

(P-P = diphosphine) was performed with 5-95% optical yields. High (> 80%) optical yields were observed with N-acetyl-α-aminoacrylic acids and itaconic acid as substrate [136].

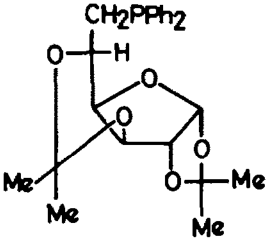
Heterogeneous catalytic asymmetric hydrogenation of acetylacetone with Raney Ni catalyst modified with R,R- or S,S-tartaric acid was used for the preparation of both enantiomers of the chiral diphosphinite (32).



$$\underset{Ph_2PO}{\overset{CH_3}{{}^{*}CH}}-CH_2-\underset{OPPh_2}{\overset{CH_3}{{}^{*}CH}}$$

32

This phosphinite was used as ligand for the asymmetric homogeneous hydrogenation of e.g. Z-α-benzamido cinnamic acid (optical yield 78%) [137]. The sugar phosphine (33) and phosphinite (34) derivatives were used as chiral ligands in the asymmetric hydrogenation of unsaturated carboxylic acids with $Rh_2(COD)_2Cl_2$. An optical yield of 62% was achieved in the case of tiglic acid [138]. The two chiral aminophosphines (35) and (36) were prepared from ornithine and used in form of their Rh(I) complexes $[Rh(COD)(L)](ClO_4)$ for the asymmetric hydrogenation of α-acylaminoacrylic acids. Optical yields between 45-84% were obtained. The two ligands behaved very similarly [139].



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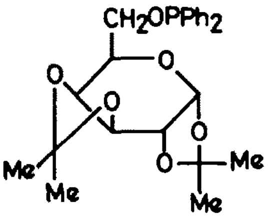

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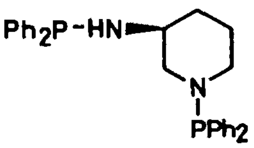

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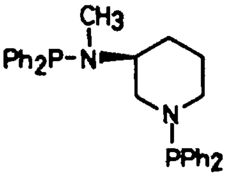
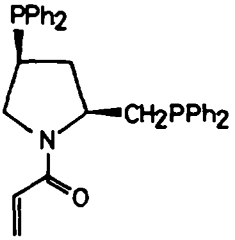


36

Copolymerization of (37) and (38) with hydrophilic comonomers and a divinyl monomer provided cross-linked insoluble polymers containing 3-5% of (37) or (38) which would swell in polar solvents. Exchange of Rh(I) in the form of $Rh_2(1,5\text{-hexadiene})_2Cl_2$ or $Rh_2(COD)_2Cl_2$ into the polymers provided catalysts which were active for the asymmetric hydrogenation of N-acetyl dehydro phenylalanine and some ring-substituted derivatives in high optical yields (86-95%) [140] . When the acrylates (39)-(41) were copolymerized with (37) the analogous Rh catalysts afforded generally small enantiomeric excesses. These varied with the structure of the pendant alcohol suggesting the participation of the polymer-bound alcohol at the catalyst site to provide an alcohol-like environment [141]. Eleven different chiral ditertiary phosphines were tested as ligands for the asymmetric hydrogenation of the (Z)- and (E)-isomers of (43)



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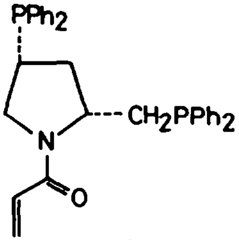

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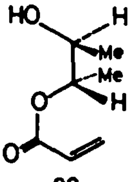

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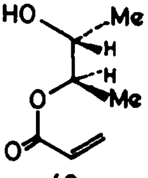

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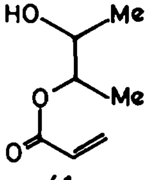

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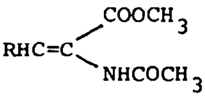
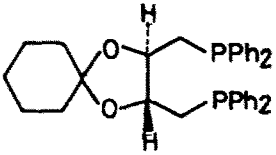


$$\mathrm{RHC{=}C}\begin{matrix}\diagup\,\mathrm{COOCH_3}\\ \diagdown\,\mathrm{NHCOCH_3}\end{matrix}$$

43

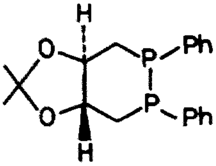
$R = CH_3OCH_2$, Pr, iPr

with rhodium complexes as catalysts. With phosphines in which two achiral P atoms are connected by a chiral C_4-unit, (E)-substrates give higher optical yields. If the two P-atoms are connected by a chiral C_2-unit, (Z)-substrates are preferred [142]. $[Rh(COD)L_2](ClO_4)$ complexes [L = (S)-(-)-4-$MeC_6H_4SO_2NHCHEtCH_2PPh_2$, (+)-P(nmen)$Ph_2$; L_2 = 44] were used as catalysts for the asymmetric hydrogenation



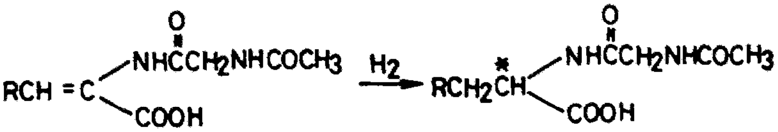
44

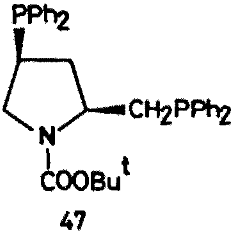
of PhCH=C(NHR)CO_2H (R = Ac, PhCO). The enantioselectivity was 6, 21 and 61%, respectively [143]. With complexes prepared from (-)-cycloDIOP (45) and $Rh_2(C_2H_4)_4Cl_2$ <u>in situ</u> 79% optical yield was achieved in hydrogenation of Z-α-acetamido cinnamic acid [144].



45

Asymmetric hydrogenation of dehydropeptides of type (46) was performed with <u>in situ</u> catalysts prepared from $Rh_2(NBD)_2Cl_2$ and the chiral phosphines (+)-DIOP (3a), (-)-BPPM (47) and R,R-trans-bis-diphenylphosphinocyclohexane (48):

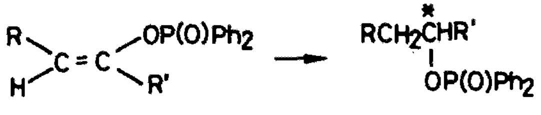




47

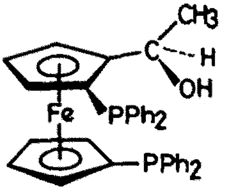
48

27-63% yields were achieved [145]. Asymmetric hydrogenation of enol phosphinates (49) to secondary alkyl phosphinates (50) was achieved with in situ cationic Rh catalysts prepared from $[Rh(NBD)_2](ClO_4)$ and the chiral phosphines (R)-(S)-BPPFOH (51),(-)-DIOP (3b) or BPPM (47). Optical yields range between 16 and 78% [146].



49 50

R = Ph, iPr, nC_6H_{13}, tBu
R' = H, Me



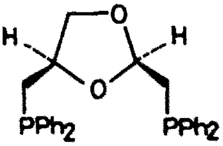
51

HRh[(+)-DIOP]$_2$ catalyses the hydrogenation of prochiral olefins under mild conditions (20-60°C, 1 atm H_2) and gives products of the same chirality as corresponding in situ 1:1 Rh(I)/(+)-DIOP catalysts, although reaction rates and optical yields are lower with the bis(diphosphine) system. A mechanism via a HRh(DIOP)(DIOP') species containing monodentate DIOP' has been proposed [147]. α-Acylaminocinnamic acids and esters were hydrogenated with $[Rh(COD)(DIOXOP)](ClO_4)$ as a chiral catalyst (DIOXOP = 52):

$$PhCH{=}C(NHCOR')COOR + H_2 \longrightarrow PhCH_2\overset{*}{C}H(NHCOR')COOR$$

R = H, Me, Et, iPr, tBu, CH_2CF_3, 1-adamantyl

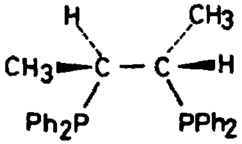
R' = H, Me, Et, iPr, tBu, Ph, 1-adamantyl



52

The best optical yields (up to 79%) were achieved with the Z-acids in the presence of Et_3N; the esters were reduced with low optical yields. Increasing the steric bulk of the enamide moiety had only a small effect on enantioselectivity [148]. An increase in reaction temperature (25 → 100°C) and the addition of a primary amine improves the enantioselectivity of the catalyst for the hydrogenation of Z-α-acetamido cinnamic acid. The effect of amine is proportional to its basicity [149]. The reduction of various dehydropeptides, gives the corresponding dipeptides with high stereoselectivity, especially when derived from an (S)-aminoacid [150]. The complexes $[Rh(COD)L_2](ClO_4)$ $[L_2 = 52, Ph_2P(CH_2)_nPPh_2$ (n = 2-6)] have been used as catalysts for the hydrogenation of Z-α-acetylaminocinnamic acid and the competitive reduction and isomerization of E-α-benzoylaminocinnamic acid. Intermediates in catalytic hydrogenation have been identified by NMR. DIOXOP (52) complexes may give rise to both dihydrides and solvates during the reaction cycle [151].

Comparison of c.d.spectra confirms that the isolated diastereomer of the catalyst substrate adduct in the $Rh(chiraphos)^+$-catalyzed hydrogenation of ethyl (Z)-α-acetamidocinnamate is also the major diastereomer in solution (chiraphos = 53) [152]. The asymmetric homogeneous hydrogenation catalyst solution obtained



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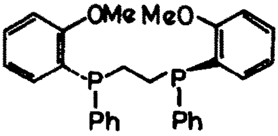
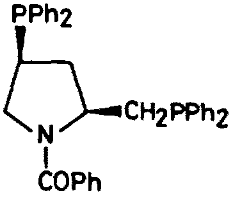


54

from $Rh(diPAMP)(COD)^+$ and H_2 in MeOH was investigated by using extended X-ray absorption fine structure (EXAFS)(diPAMP = 54). The first shell coordination environment about the rhodium atoms consists of two phosphorous and two oxygen atoms, presumably from coordinated solvent methanol. When the substrate α-(acylamino) cinnamic acid is added to this MeOH solvated species $Rh(diPAMP)(CH_3OH)_2^+$ two distinct Rh-P distances appear, one trans to an oxygen and one trans to the olefin [153]. The reaction of

[Rh(diene)(biphosphine)](BF_4) complexes catalyst precursors for asymmetric hydrogenation with 1 atm H_2 in MeOH or other polar solvents has been studied. The initial product is a solvated dihydride or a solvate, depending on phosphine structure. With (R)-phenyl bis-diphenylphosphino ethane the formation of dimers and in the presence of Et_3N that of trimers has been observed [154]. The complexes formed by hydrogenating [Rh(diene)(BPPM)](BF_4) or [Rh(diene)(BZPPM)](BF_4) and adding dehydroaminoacids or itaconic acid derivatives in MeOH solution were investigated by their ^{31}P NMR spectra. The BPPM (47) and BZPPM (55) complexes, while showing very close similarities in hydrogenation experiments, seem to interact rather differently with unsaturated substrates [155]. The asymmetric hydrogenation of β-methylene acids with Rh-BPPM complex catalysts is proposed to proceed via intermediate (56) [156]:



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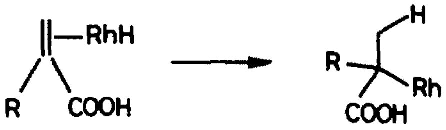

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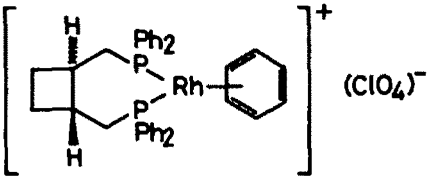
The complex (57) has been prepared and its structure determined:



57

The observed structure illustrates one way in which benzene - a solvent often used in homogeneous hydrogenations - may coordinate to the Rh(I)-phosphine complexes used as catalyst. Its THF-benzene solutions are catalytically active for hydrogenation [157]. Rates and activation parameters have been determined for solvent exchange with complexes of the type $[H_2M(PR_3)_2(solv)_2]^+$ (M = Rh, Ir; R = Ph, Cy; solv = MeCN, Me_2CO). The coordinated solvent molecules are in trans positions with respect to the hydride ligands. At 298K the rate constants for solvent exchange differ by a factor of 10^7. The least reactive is MeCN and the most reactive is Me_2CO [158].

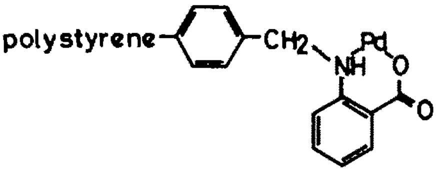
Ziegler-Natta type catalysts prepared from $LiAlH_2(OR)_2$ (R = $MeOCH_2CH_2$ or tBu) and cyclopentadienyl Ti(IV) complexes in which a (men) or (nmen) group is located on the cyclopentadienyl ring can be used as enantioselective catalyst for the hydrogenation of prochiral olefins. The best optical yields (25-28% with 2-phenyl-1-butene) were achieved with $Ti(menCp)_2Cl_2$ and $Ti(Cp)(menCp)Cl_2$, complexes containing the (nmenCp) ligand were less effective [159].

4. Hydrogenation of Dienes and Acetylenes

a) Pd and Pt Catalysts

The hydrogenation of cyclopentadiene and PhC≡CH with a $[Pd_5(PhP)_2]_4$ catalyst in DMF involved equilibrium complexation of the substrate with the catalyst, followed by rate determining hydrogenolysis of the Pd-C bond in the complex to form the olefin product and regenerate the catalyst [160]. Allylmetal-sulfur clusters of the type $[(\eta^3\text{-}C_3H_5)MS(\eta^3\text{-}C_3H_5)M^1]_x$ (M,M^1 = Ni, Pd, Pt) catalyze the hydrogenation of hexyne-3 under ambient conditions. The pure Pd clusters and the mixed Pd-Pt cluster are catalysts for alkyne to cis-alkene hydrogenation and for alkene isomerization, the pure Pt cluster is a non-selective alkyne and alkene hydrogenation catalyst. The active species in these reactions are unlikely to be single atoms [161]. Reduction of Pd complexes with amine or sulfide ligands by organoaluminium compounds gave active and selective catalysts for the hydrogenation of conjugated dienes to olefins. The activity of catalysts increased when H_2O or O_2 was added as an activator [162]. Metal complex catalysts prepared by the reaction of $NaBH_4$ with an aqueous solution of $PdCl_2$, $NiCl_2$ or $RhCl_3$ and a chelating amine e.g. bpy or polyethyleneimine, catalyze the hydrogenation of 1,3-cycloalkadienes, butadiene and 1-hexyne to olefins [163]. Complexes of $PdCl_2$ with amines or py were reduced with $(iBu)_2AlH$ and then used to catalyze the selective hydrogenation of conjugated dienes into olefins in aromatic solvents. The reaction is promoted by H_2O and O_2 [164]. Among several group VIII metal catalysts for the hydrogenation of $PhC\equiv CPh$ the most selective for cis--stilbene formation was $PtCl_2(SnCl_3)_2^{2-}$ and the least selective was Py_3RhCl_3 + $NaBH_4$. The lower selectivity resulted from the competing hydrogenation of cis-stilbene [165].

A polystyrene-bound Pd complex (58)was prepared by treating chloromethylated polystyrene with anthranilic acid and $PdCl_2$, and used as catalyst for the cis hydrogenation of alkynes. The catalyst is less reactive than the Lindlar catalyst for hydrogenation but is stable to air and storage [166]. $PdCl_2$ was anchored to phosphinated crosslinked polystyrene by substitution of the py ligand in $Cl_2Pd(py)_2$ with the polymeric phosphine. This complex was tested as catalyst for hydrogenation of soybean oil under ambient conditions [167].



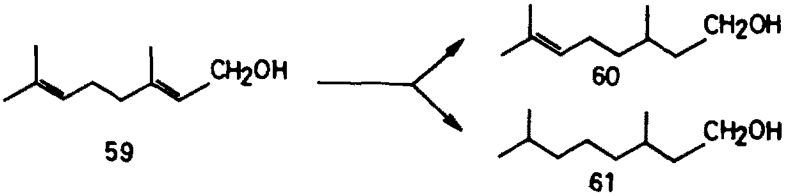
58

b) Rh and Ir Catalysts

Cationic Rh(I) complexes of type $[Rh(NBD)L_2](ClO_4)$(L_2 = diphos or L = PPh_3) were studied for the hydrogenation of soybean oil at 30° and 1 atm. These catalysts give a good yield of products with cis-configuration [168]. $Rh[P(o\text{-}tol)_3]_2Cl_2$ and $Rh(PCy_3)_2Cl_2$ are catalysts for the hydrosilylation of alkenes, alkynes, ketones and α,β-unsaturated carboxylic acid esters. Both complexes become catalysts for hydrogenation of alkenes and alkynes when activated by Et_3Al [169].

Pentynes are hydrogenated to pentenes in the presence of $Rh_4(CO)_{12}$ or $Rh_2(CO)_4Cl_2$ in homogeneous toluene solution. If these complexes are anchored on γ-Al_2O_3, complete hydrogenation to pentane is favoured [170]. $Rh_2(CO)_4Cl_2$ hydrogenates trans-1,3-pentadiene at 60-80°C and 1 atm H_2 both in toluene solution and anchored on Al_2O_3 to trans-2-pentene as main product. CO and PPh_3 inhibit the reaction [171]. Supported Rh complexes, prepared from polystyrene-bound py and bpy ligands, Ⓟ-py and Ⓟ-bpy, and the dimers $Rh_2(CO)_2(X)_2Cl_2$ (X = CO, PPh_3 or $P(p\text{-}tol)_3$), as well as Ⓟ-bpy $PdCl_2$ and Ⓟ-bpy $PtCl_2$ were investigated as hydrogenation catalysts. In case of the former two systems metal aggregates were formed. The (Ⓟ-bpy)$PtCl_2$ system is an active catalyst for the hydrogenation of terminal alkenes and alkynes. Metal formation did not occur [172]. Rh(NBD)(diphos)$^+$ intercalated in hectorite, a swelling layered silicate, catalyzes the hydrogenation of butadiene, isoprene and 2,3-dimethylbutadiene. In acetone or MeOH as solvents (in which the interlayers are swollen beyond the dimensions of the intercalate) the rates range from 0.08 to 0.83, relative to the homogeneous catalyst [173].

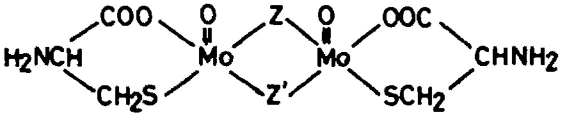
Hydrogenation of geraniol (59) to citronellol (60) and 3,7-di-methyloctanol (61)



was investigated with Ir and HIr$(PPh_3)_3Cl_2$ catalysts. The results suggest that both (60) and (61) are formed from (59) through a common intermediate. The activity of HIr$(PPh_3)_3Cl_2$ for hydrogenations of (59), allyl alcohol and diethyl fumarate was increased by the addition of H_2O_2 [174].

c) Cr, Mo, Co, Fe and Ru Catalysts

The silica-bonded complex prepared by reacting polyphenylsiloxane with silylated chromosorb and then with $Cr(CO)_6$ catalyzed the stereoselective hydrogenation of methyl sorbate [175]. The catalytic activity of benzene chromium tricarbonyl for the hydrogenation of methyl sorbate and the addition of CCl_4 to cyclooctene is increased by substituents with an α-heteroatom (O,N) on the benzene ring [176]. The catalytic activity of the Mo cysteine complexes (62-64)



62 Z = Z' = O

63 Z = S, Z' = O

64 Z = Z' = S

in the hydrogenation of C_2H_2 was studied. C_2H_4/C_2H_6 ratios of 20-25, 8-10 and 4-5 were obtained with (62), (63) and (64), respectively [177].

Catalyst systems prepared from $CoCl_2$, KCN and ethylenediamine (or bpy) at a 1:3:1 ratio under H_2 in a two-phase solvent mixture (H_2O/CH_3OH and benzene) have been investigated for the hydrogenation of conjugated dienes into monoenes. Phase transfer reagents had little effect on reaction rate or product distribution [178]. In the hydrogenation of 2,4-hexadienoic acid to 2-hexenoic acid by pentacyanocobaltate(III)hydride, neutral surfactant micelles enhanced the rate by a factor of 3; anionic and cationic surfactant micelles totally inhibited the reaction [179]. The hydrogenation of Me esters of unsaturated acids of soybean oil proceeded readily at 20-80° in the presence of a $Co(acac)_3 + Et_3Al$ or $Co(acac)_3 + NaAlH_2(OCH_2CH_2OMe)_2$ catalyst system. The optimal Al:Co ratios were around 30:1 [180].

A $Et_3Al + FeSt_3$ catalyst (Al:Fe = 5:1) was used for hydrogenation of sunflower oil at 60-80° [407]. $Ru(PPh_3)_2(SnCl_3)Cl$ catalyzed the hydrogenation of 1-hexene, 1,3-pentadiene, and 1-hexyne. The activity and selectivity of the mixed complex was higher than that of $Ru(PPh_3)_2Cl_2$ [181]

The reaction of $Ru_3(CO)_{12}$ with t-butylacetylene gives $HRu_3(CO)_9C_2Bu^t$. This complex reacts with H_2 in refluxing octane to give $H_3Ru_3(CO)_9CCH_2CMe_3$ and, upon further hydrogenation, $H_4Ru_4(CO)_{12}$ and neo-hexane. The yield of alkane is low and some decomposition to metal is also observed [182].

5. Hydrogenation of Arenes

The η^3-$C_3H_5Co[P(OMe)_3]_3$- catalyzed hydrogenations of cyclohexenes, cyclohexadienes and arenes with D_2 have been investigated. Complete cis stereoselectivity was observed in the addition of D_2. When alkyl-substituted arenes where reduced with D_2, the hydrogen atoms in the alkyl chains also underwent H-D exchange. $HCo[P(OMe)_3]_2$ is probably the true catalytic species [183]. The η^3-cyclooctenyl complexes $C_8H_{13}Co[P(OR)_3]_3$ (R = Me, Et, iPr) catalyze the hydrogenation of benzene with an activity comparable to that of the corresponding allyl complexes. The structure of the R = Me complex has been determined [184].

Polystyrene-supported $RhCpCl_2$ is a hydrogenation catalyst for olefins, ketones and arenes in the presence of excess Et_3N under 8 atm H_2 at 70°C [185]. Silica-bound rhodium hydride complexes SIL-ORh(allyl)H catalyze the hydrogenation of arenes at 22°C and 500 psi H_2; for benzene the initial rate was 410 turnovers/h and no decrease in rate was observed even after >3000 turnovers [186]. A set of styrene + chloromethylstyrene + divinylbenzene macroporous copolymers was phosphinated and treated with $Rh_2(CO)_4Cl_2$ or $Rh(PPh_3)_3Cl$. The activity for benzene hydrogenation was linked to the formation of metallic particles but in the case of hexene as substrate the results suggest the existence of several types of active sites [187].

6. Hydrogenation of the Carbonyl Group

a) Aldehydes and Ketones

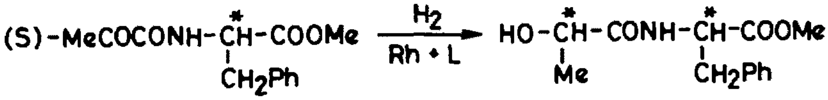
Catalytic hydrogenation of aldehydes with $[Rh(NBD)(PR_3)_2](ClO_4)$ was investigated at 30°C under 1 and 50 atm of H_2. The highest activity among the ligands examined was found for PEt_3. Aldehydes are decarbonylated during the reaction and this leads to deactivation of the catalyst, especially under atmospheric pressure [188]. $HRu(CO)(PPh_3)_3Cl$ and several other Ru complexes catalyze the reduction of aldehydes to the corresponding alcohols in toluene solution under mild reaction conditions (30 atm H_2, 60-140°C). Turnover numbers up to 32000 have been achieved [189]. Based on a kinetic analysis of earlier measurements $H_3Co(CO)_2$ has been proposed as the active catalyst for aldehyde hydrogenation by $HCo(CO)_4$ under hydroformylation conditions [190].

Aldehydes and ketones were hydrogenated at 160°C and 15 atm H_2 with $Ru(CO)_2(PPh_3)_2Cl_2$ in solution and in the gas phase with the catalyst in a supported liquid phase. The catalytic activities were nearly equal [40]. The catalytic hydrogenation of several ketones with cationic Rh complexes prepared in situ from $[Rh(NBD)(PR_3)_2](ClO_4)$ has been investigated at 30°C with H_2 at atmospheric pressure. Et_3P gave the highest activity among the ligands used. An electron-withdrawing substituent in the ketone was found to increase its reactivity among both alkyl and aryl ketones; alkyl ketones generally reacted faster. Unsaturated ketones were hydrogenated to yield saturated ketones first, no unsaturated alcohol was observed [191]. The catalytic efficiency of Amberlite-supported Rh(I) chiral diphosphine complexes for asymmetric hydrogenation of $RCOR^1$ (R = Ph, Me; R^1 = Me, Et, Pr, Bu, nC_6H_{13}) was similar to that of the $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ cluster or the $Rh_2(C_2H_4)_4Cl_2$ + (-)-DIOP (3b) system. Asymmetric induction increased with the bulkiness of the alkyl groups in the ketones [192].

Cobalt carbonyls containing bis tertiary phosphines were more active catalysts than $Co_2(CO)_8$ for the hydrogenation of α,β-unsaturated ketones and aldehydes under hydroformylation conditions [193]. The hydrides $H_3Ir(PPh_3)_3$ and $H_5Ir(PPh_3)_2$ catalyze the hydrogenation of ketones and that of the C=C and C=O groups of α,β-unsaturated ketones in CF_3CO_2H. An ionic mechanism, including H^- transfer from the Ir complex to the protonated ketone, is proposed [194].

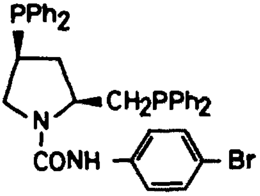
b) Other Carbonyl Compounds

The hydro(phosphine)ruthenate complexes $K[H_2Ru(Ph_3P)_2Ph_2PC_6H_4]\cdot C_{10}H_8\cdot Et_2O$ and $K_2[H_4Ru_2(Ph_3P)_3(Ph_2P)]\cdot$diglyme are homogeneous catalysts for the hydrogenation of ketones and aldehydes (85°C, 6.2 atm H_2), carboxylic acid esters and nitriles (90°C, 6.2 atm H_2). This represents the first instance of a homogeneous catalytic hydrogenation of a simple aliphatic ester [195]. Asymmetric hydrogenation of (65) with Rh(I) complexes containing different chiral [(+) and (-) DIOP (3b), BPPM (47), p-Br-C_6H_4-CAPP (66)] and achiral (PPh_3) ligands led to practically the same extent of asymmetric induction:



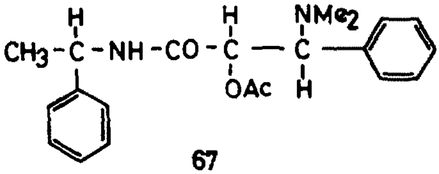
$$(S)\text{-}MeCOCONH\text{-}\underset{CH_2Ph}{\overset{*}{C}H}\text{-}COOMe \xrightarrow[Rh + L]{H_2} HO\text{-}\underset{Me}{\overset{*}{C}H}\text{-}CONH\text{-}\underset{CH_2Ph}{\overset{*}{C}H}\text{-}COOMe$$

65



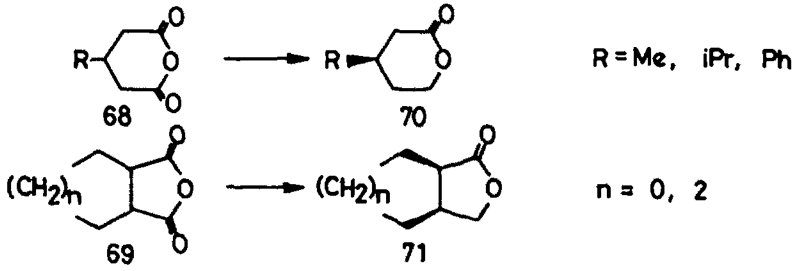
66

Accordingly only asymmetric induction arising from the chiral center of (65) takes place and the Rh catalyst bearing a chiral ligand does not act as a chiral catalyst at all in this case [196]. (67) Was used as a new type of chiral cocatalyst in the Co(dmg)$_2$ + chiral cocatalyst system for asymmetric hydrogenation of methyl(α-acetamido)-acrylate and benzil. The optical yield reached 34.5% [197].



67

Cyclic anhydrides with a prochiral carbon atom (68) or with a meso configuration (69) are reduced to chiral lactones with a $Ru_2Cl_4(DIOP)_3$ catalyst at 100°C and 10 atm H_2. With (-)-DIOP (3b) as ligand the lactones (70) and (71) were obtained containing the (R) and (1R,2S) enantiomers respectively, in 5-20% excess [198].



The η^2-acyls $U(C_5Me_5)_2(COPh)Cl$ and $Th(C_5Me_5)_2(COCH_2Bu^t)Cl$ react with H_2 at 0.75 atm and 35°C in the presence of $[H_2Th(C_5Me_5)_2]_2$ as catalyst to yield the corresponding alkoxides $U(C_5Me_5)_2(OCH_2Ph)Cl$ and $Th(C_5Me_5)_2(OCH_2CH_2Bu^t)Cl$. The system was run for 50 turnovers with negligible degradation of the catalyst [199]. The $RCOCCo_3(CO)_9$ complexes (R = H, alkyl, aryl) undergo reduction with H_2 in refluxing benzene with no added catalyst at atmospheric pressure to produce the respective $RCHOHCCo_3(CO)_9$ and, in some cases like R = H, the completely reduced $RCH_2CCo_3(CO)_9$ complexes. The reduction to alcohol is reversible [200].

c) Reduction of CO_2

Cu and Pd complexes with $Ph_2PCH_2PPh_2$ catalyze the reduction of CO_2 by H_2 at 120°C and 30 atm (CO_2:H_2 = 1:1) in an EtOH/Et_3N solvent mixture. The products are ethyl formate, methane and sometimes small quantities of diethyl oxalate. The most active complex was $Pd(Ph_2PCH_2PPh_2)_2$ [201]. With $Rh_4(CO)_{12}$, $Rh_2(CO)_4Cl_2$ or $Rh(Ph_3P)_3Cl$ as catalyst CO_2 is reduced to CO in presence of $AlBr_3$ and H_2. Traces of C_1-C_5 alkanes were also formed. $Rh(PPh_3)_3Cl$ was not converted to a carbonyl complex [202].

7. Hydrogenation of Nitro Compounds

$(C_3H_5)Pd(L)Cl$ and $Rh(CO)L_2Cl$ (L = sugar amido phosphite) were prepared and tested as hydrogenation catalysts for $PhNO_2$ and [203]. The hydrogenation of $PhNO_2$ by the complex obtained from $Pt(DMSO)_2Cl_2$ and $NaBH_4$ in DMSO is accelerated by quinones in aprotic solvents. According to the proposed mechanism hydroquinones are formed and act as proton donors [204]. The Rh complex of the anion-radical of potassium indigodisulfonate (A) is an active catalyst for the hydrogenation of $PhNO_2$. The kinetics of the stoichiometric reduction of $PhNO_2$ by (A) has been investigated. The results support a direct electron transfer from indigosulfonate ion-radical to $PhNO_2$ without interaction of the inner coordination sphere of Rh [205]. The 1:1 complex of $(NH_4)_2IrCl_6$ with chloroanilic acid is a homogeneous catalyst for the hydrogenation of RNO_2 (R = o-, m- and p-ClC_6H_4, 2,5- and 3,4-$Cl_2C_6H_3$) to give RNH_2 in high yield [206].

8. Miscellaneous Hydrogenations

Coordination polymers prepared from 2,3,6,7-octateraone tetraoxime and $Pd(PhCN)_2Cl_2$ catalyze the hydrogenation of alkanes, alkynes, carbonyl compounds, azobenzene, and other substrates [207]. Polymer-Ru complexes have been prepared by reacting Ru(COT)(COD) with polystyrene under H_2, whereby the two cyclo-olefinic ligands are displaced by the phenyl rings of the polystyrene. These complexes exhibit catalytic activity at 25-80°C and 50 atm H_2 for the hydrogenation of olefins, aromatic hydrocarbons, ketones, oximes and nitro derivatives. At 120-140° nitriles are converted into amino derivatives [208].

Styrene oxide was catalytically hydrogenated to β-phenylethyl alcohol and phenylacetaldehyde with cationic Rh complexes of the type $Rh(NBD)(PR_3)_2$ (ClO_4) (R = Ph, Et). No α-phenylethyl alcohol or acetophenone were formed, but 20-40% of the oxide was converted to oligomeric products. The hydrogenation did not proceed in the absence of water [209]. $K_3[Co(CN)_6]$ catalyzed the hydrogenolysis of benzyloxycarbonyl and benzyl ester protective groups from amino acids and peptides. Benzyl ether groups were unaffected. Yields were ≫90% in the case of alanine derivatives [210].

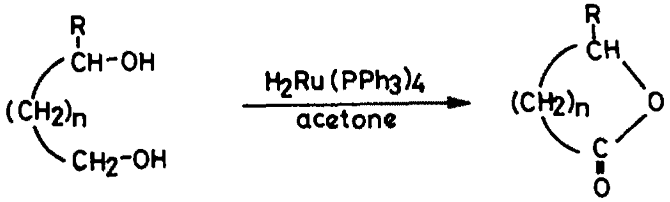
9. Dehydrogenation of Alcohols

$Ru(PPh_3)_3Cl_2$ in benzene dehydrogenates primary alcohols selectively to aldehydes in the presence of secondary alcohols at 250°C. The reaction requires 0.5 mol of $Ru(PPh_3)_3Cl_2$ for one mol of alcohol. $HRu(PPh_3)_3Cl$ is formed as an intermediate and this complex is still capable of dehydrogenating one mole alcohol [211]. trans-$Mo(N_2)_2(diphos)_2$ stoichiometrically dehydrogenates primary alcohols to aldehydes (which are successively decarbonylated to hydrocarbons), secondary alcohols to ketones, and indoline to indole in benzene solution at reflux temperature. $H_4Mo(diphos)_2$ is formed [212].

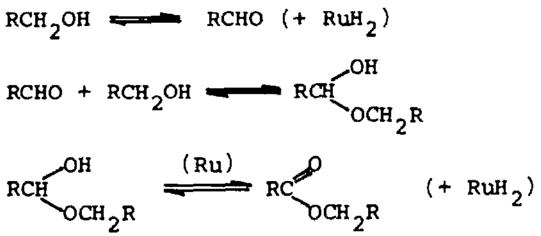
Catalytic systems have also been described for this reaction. The reaction is catalyzed at the boiling point of the alcohol by $Ru(CO)(PPh_3)_2(OOCCF_3)_2$ and by this complex attached to polystyrene functionalized with phosphine groups, carboxylic groups or both. Rate data indicate a similar reaction mechanism for all four catalysts [213]. $Rh(PPh_3)_3Cl$ catalyzes the dehydrogenation of isopropyl alcohol under photo-irradiation at room temperature. This complex was found to be more active than other Rh complexes investigated previously, especially if the reaction mixture was prepared in the presence of oxygen [214]. Dehydrogenation of 2-butanol over various poly(metal phtalocyanine) catalysts (Poly-M-Pc) was studied by a continuous flow system under atmospheric pressure. Catalytic activity of Poly-Pt-Pc was higher than that of Pt/silicagel [215]. $Rh_2(OAc)_4$, immobilized on Ph_2P-modified silica surface, catalyzes the dehydrogenation of iPrOH [216].

The homogeneous catalytic condensation of alcohols to esters and diols to lactones has been accomplished using $H_2Ru(PPh_3)_4$ as catalyst at 180°C. The yield of lactones is significantly increased if the reaction is carried out in the presence of 3 molar equivalents of acetone as a H acceptor:

$$2\ RCH_2OH \xrightarrow{H_2Ru(PPh_3)_4} RCOOCH_2R + 2\ H_2$$



The following mechanism involving two dehydrogenation steps catalyzed by the Ru complex has been proposed for these reactions [217]:



$$RCH_2OH \rightleftharpoons RCHO\ (+\ RuH_2)$$

$$RCHO + RCH_2OH \rightleftharpoons RCH(OH)(OCH_2R)$$

$$RCH(OH)(OCH_2R) \underset{}{\overset{(Ru)}{\rightleftharpoons}} RC(=O)OCH_2R \quad (+\ RuH_2)$$

10. H-transfer Reactions

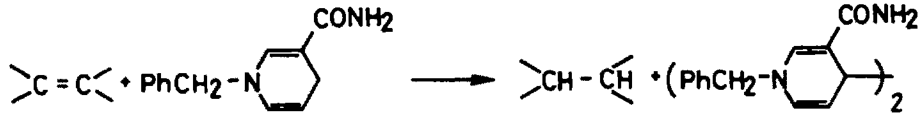
a) Hydrogenation of C=C and C=O Bonds

Ketones are reduced under mild conditions to the corresponding alcohols by secondary alcohols in homogeneous bulk H-transfer reactions catalyzed by $Ru(CO)(Ph_3P)_3(OOCCF_3)_2$ at 140°. The reactions are reversible. The rate determining step is the dehydrogenation of the alcohols. Conversions can be described by the rate law of a reversible second-order reaction [218]. A kinetic and spectroscopic study of the H-transfer from alcohols to benzylideneacetone catalyzed by $Ru(PPh_3)_3Cl_2$ at 170-190° showed that the complex is transformed by alcohols into $H_2Ru(CO)(PPh_3)_3$ which hydrogenates the olefin. The rate determining step is considered to be the transfer of H from the alcohol to a Ru species [219]. Complexes formed by adding Group Vb ligands to $[Rh(NBD)_2](ClO_4)$ in the presence of KOH catalyze H-transfer from iPrOH to acetophenone and olefins at reflux temperature [220]. trans-Mo(N_2)$_2$(diphos) and analogous Mo complexes catalyze the H-transfer from alcohols to ketones and olefins in refluxing benzene solutions. The hydrogenation of olefins is inhibited by N_2 [221]. The reduction of prochiral ketones by H-transfer from iPrOH is catalyzed by complexes of the type [Ir(COD)L](ClO_4) (L = chiral Schiff bases like 2-pyridinalphenylethylimine or 2-piridinal-3-(iminomethyl)pinane). Optical yields up to 33% have been achieved [222].

Ir(CO)(PPh_3)$_2$Cl anchored on a styrene-divinylbenzene copolymer is a highly stable and active catalyst for the transfer hydrogenation of α,β-unsaturated ketones by formic acid (t = 97°C):

$$RCH{=}CHCOR' + HCOOH \longrightarrow RCH_2CH_2COR' + CO_2$$

The immobilized complex is more efficient than free Ir(CO)(PPh_3)$_2$Cl and its activity increases after repeated reuse [223]. Irradiation of a solution of Ru(bpy)$_3$Cl$_2$.6H$_2$O, an olefin and 1-benzyl-1,4-dihydronicotinamide (BNAH) at $>$470 nm resulted in the hydrogenation of the olefin by hydrogen transferred from BNAH and the formation of coupling products:



BNAH

+ olefin-BNAH cross-coupling products

This photomediated two-electron reduction proceeds by way of sequential electron transfer [224].

b) Disproportionation of Aldehydes

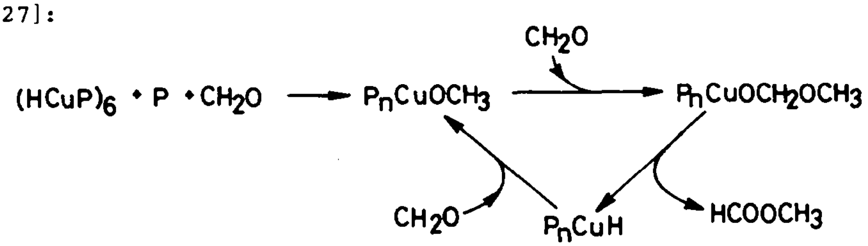
Acetaldehyde is converted into ethanol and acetic acid (1:1) by dilute neutral aqueous solutions of pentamethylcyclopentadienyl--rhodium or -iridium complexes, e.g. $[Rh(C_5Me_5)]_2(OH)_3^+$. In base (pH $>$ 12.8) the disproportionation of acetaldehyde (Cannizzaro--reaction) was $>10^4$ fold accelerated in the presence of catalyst and competed succesfully with the aldol condensation [225]. H is transferred from formaldehyde to other aldehydes (or ketones) in water under basic conditions in the presence of $[Rh_2(C_5Me_5)_2(OH)_3]Cl$:

$$RCHO + HCHO + OH^- \longrightarrow RCH_2OH + HCOO^-$$

This metal-catalyzed Cannizzaro reaction is so fast, that the base--induced aldol condensation can be entirely repressed [226]. $[HCuP(p\text{-}tol)_3]_6$ catalyses the conversion of formaldehyde to methyl formate in benzene:

$$2CH_2O \longrightarrow HCOOCH_3$$

The following mechanism has been proposed for this transition metal hydride catalysed analog of the Tishchenko reaction [$P = P(p\text{-}tol)_3$] [227]:



$Ru_3(CO)_{12}$, in the presence of diphenylacetylene catalyzes the formation of esters from primary alcohols [228]:

$$2\ RCH_2OH + 2\ PhC{\equiv}CPh \longrightarrow RCOOCH_2R + 2\ PhCH{=}CHPh$$

from alcohols and aldehydes:

$$RCHO + RCH_2OH + PhC{\equiv}CPh \longrightarrow RCOOCH_2R + PhCH{=}CHPh$$

and from benzaldehyde:

$$2\ PhCHO + PhC{\equiv}CPh \xrightarrow{water} PhCOOCH_2Ph + PhCH{=}CHPh.$$

c) Reduction of N-containing Compounds

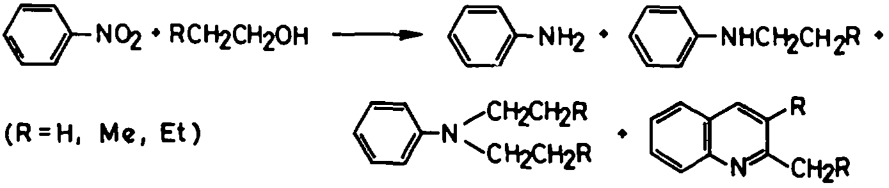
Complexes of the type $Ir(C_2H_4)_2LCl$ (L = bpy and derivatives, phen and derivatives) are catalyst precursors for the H-transfer from iPrOH to ketones and Schiff bases. The most active is the

L = 3,4,7,8-Me_4phen derivative which, at 83°C gave turnovers of up to 5000 cycles per min [229]. Aromatic aldimines have been reduced to secondary amines by transfer hydrogenation with refluxing iPrOH catalyzed by $Rh(PPh_3)_3Cl$ in the presence of Na_2CO_3:

$$\text{Ar-CH=N-Ar} \longrightarrow \text{ArCH}_2\text{NHAr} \qquad \approx 90\%$$

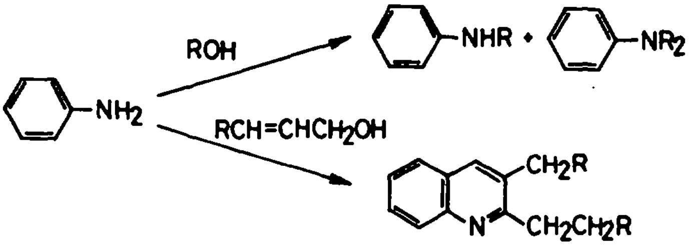
$HRh(PPh_3)_4$ was an even more active catalyst [230].

Nitrobenzene reacts with saturated alcohols in the presence of $Ru(PPh_3)_3Cl_2$ at 180°C to give N-alkylanilines and 2,3-dialkylquinolines in good yield [231]:



The reaction starts with reduction of nitrobenzene by the catalytic hydrogen transfer from the alcohols generating aniline and aldehydes:

Accordingly, aniline reacts with saturated and allylic alcohols in the presence of $Ru(PPh_3)_3Cl_2$ at 180° to give N-alkylanilines and 2,3-alkylquinolines [232]:



Photolysing a $Ru(bpy)_3^{2+}$ + ascorbate system in the presence of added bpy gave H_2bpy in more than 50% yield:

$$H_2A + bpy \xrightarrow{h\nu} A + H_2bpy$$

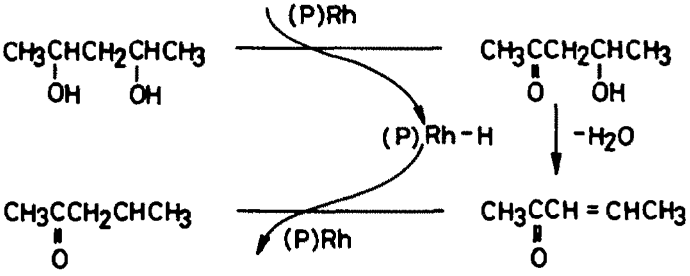
(H_2A = ascorbic acid). Some H_2 is also formed and its yield is dramatically increased if Co^{2+} is added to the system. The main overall reaction is in this case

$$H_2A \xrightarrow{h\nu} A + H_2$$

which involves net energy storage [233].

d) Intramolecular H-transfer

In the presence of $RhCl_3/PPh_3$ catalysts 1,3-diols are transformed to monoketones. The following mechanism has been proposed for this reaction [(P) = phosphine ligands] [234]:



11. Reductions without Molecular H_2

a) Transition Metal Hydrides

Direct reduction of amides to alkanes was carried out using $(HTiCp_2)_x$ or $(TiCp_2)_{1-2}$. Thus, treating $n\text{-}C_{11}H_{23}CONHR$ [R = Ph, p-tol, p-anisyl, 2,4-$(MeO)_2C_6H_3$] with $HTiCp_2$ in ether at room temperature for 4-6 h yielded 24-40% $n\text{-}C_{12}H_{26}$ [235]. Rates of reaction of $HMCp(CO)_3$ (M = Mo, W) with α-methylstyrene have been determined. The rate law is first order in olefin and in hydride and an inverse isotope effect is observed with the deuterides. A radical mechanism is suggested [236]:

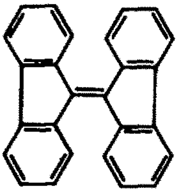
$$HMCp(CO)_3 + \underset{CH_3}{\underset{|}{PhC}}=CH_2 \rightleftharpoons \dot{M}Cp(CO)_3 + Ph\dot{C}(CH_3)_2$$

$$HMCp(CO)_3 + Ph\dot{C}(CH_3)_2 \rightleftharpoons \dot{M}Cp(CO)_3 + PhCH(CH_3)_2$$

$$2\,\dot{M}Cp(CO)_3 \rightleftharpoons M_2Cp_2(CO)_6$$

$HOs_3(CO)_9L$ (L = CO, PMe_2Ph) reacts with CF_3CN to give $HOs_3[\mu-\eta^2-C(CF_3)NH](CO)_9L$ and $HOs_3[\mu-\eta^1-NCH(CF_3)](CO)_9L$. In each, one hydride ligand was transferred to the nitrile ligand, which could be viewed as the first step of hydrogenation of a nitrile at a polynuclear center [237, 238].

9,10-Dimethylanthracene reacts with $HMn(CO)_5$ at 100° to yield a nearly equimolar mixture of cis- and trans- 9,10-dihydro-9,10--dimethylanthracene. Experiments support a free-radical mechanism in which the rate determining step is the transfer of H from $HMn(CO)_5$ tc 9,10-dimethylanthracene [239]. The relative rates of stoichiometric hydrogenation of several phenylalkenes with $HCo(CO)_4$ were measured. Compared to 1,1-diphenylethylene, 1,1-diphenylpropene reacts more than 200 times slower, but when the two olefins are mixed, the rate of hydrogenation of 1,1-diphenylpropene is increased about 100 fold. A mechanism is proposed [240]. The stoichiometric hydrogenation of several highly substituted ethylene derivatives with $HCo(CO)_4$ has been studied. Most substrates react very slowly with $HCo(CO)_4$ indicating considerable steric effects.



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α-Phenylacrylonitrile and bifluorenylidene (72), however, react very rapidly, which is consistent with radical type intermediates [241]. $(PPh_3)_2Cu(BH_4)$ reduces carbonyl compounds to alcohols in the presence of acid catalysts (HCl gas in CH_2Cl_2) with excellent yields. The reduction is highly stereoselective, e.g. in the reduction of 3,3,5-trimethylcyclohexanone the alcohol is 84% trans. α,β-Unsaturated aldehydes are reduced regioselectively to allylic alcohols and in a mixture of an aldehyde and a ketone, an aldehyde may be reduced preferentially [242]. Aromatic azides were reduced to the corresponding anilines in good yields with $(Ph_3P)_2Cu(BH_4)$ in $CHCl_3$ at room temperature [243].

b) Main Group Hydrides in the Presence of Transition Metal Complexes

Complex reducing agents composed of NaH, an alkoxide and a transition metal salt (Ti, V, Fe, Co, Ni, Zu, Cd, Zr, Mo, W) efficiently convert alkyl and vinyl halides to the corresponding hydrocarbons. Reductions with the nickel containing reagents are catalytic with respect to the nickel salt [244].

Ph_3AsO could be deoxygenated to Ph_3As by $TiCl_4$ and a reducing agent ($LiAlH_4$, $NaBH_4$, Zn or Mg) in refluxing THF [245]. The thermally stable and soluble mesitylcopper(I) catalyzes the 1,4-reduction of cyclohexenone by $LiAlH_4$ in THF solution. Addition of HMPA increases the selectivity of the reaction [246].

Mo(II)complexes of water-soluble polymers with cysteine residues are effective catalysts for the reduction of C_2H_2 in the presence of $NaBH_4$. Their catalytic activity is 2-3 times greater than that of corresponding Mo-cysteine complexes of low molecular weight [247]. Iodobenzene and some p-substituted derivatives may be reduced by $NaBH_4$ activated by catalytic amounts of $TiCp_2Cl_2$ or $TiCpCl_3$ in DMF. The reaction occurs only in the presence of air and not under an inert atmosphere [248]. Transition metal phtalocyanine complexes (metal = Mn^{II}, Fe^{II}, Co^{II}, Pd^{II}, $V^{IV}O$) catalyze the reduction of several functional groups by $NaBH_4$ in alcoholic solvents: nitro- and nitroso compounds, oximes, Schiff-bases and nitriles to amines, olefins and alkyl halides to alkanes. The reaction is not inhibited by thiols, CN^- or I^-, usually regarded as strong catalyst poisons. Aromatic rings, aryl halides, carboxylic esters and amides are inert under the reaction conditions (25°C) [249]. $RC_6H_4NO_2$ (R = H, pMe, m-Me, o-Me, p-Cl, p-OH, p-CO_2H, o-CO_2H) and nitronaphtalene were reduced with $NaBH_4$ + $NiCl_2$ to give the corresponding $RC_6H_4NH_2$ or 1-aminonaphtalene respectively, in 76-95% yields. Similarly, PhNO, PhN(O)Ph, PhN=NPh, and PhNHOH were reduced with $NaBH_4$ + $NiCl_2$ to give 62-78% $PhNH_2$ [250]. $ErCl_3$ catalyzes the selective reduction of conjugated aldehydes in the presence of non-conjugated ones by $NaBH_4$ in aqueous ethanol solution. The same system is useful for the reduction of ketones in the presence of aldehydes too. This latter selective reduction can be achieved also with $CrCl_3$ instead of $ErCl_3$ [251].

$Pd(PPh_3)_4$, various Pd(II) complexes, and $PdCl_2$ in the presence of PPh_3 catalyze the reduction of acyl chlorides with Bu_3SnH to give aldehydes at room temperature in very good yields:

$$RCOCl + Bu_3SnH \longrightarrow RCHO + Bu_3SnCl$$

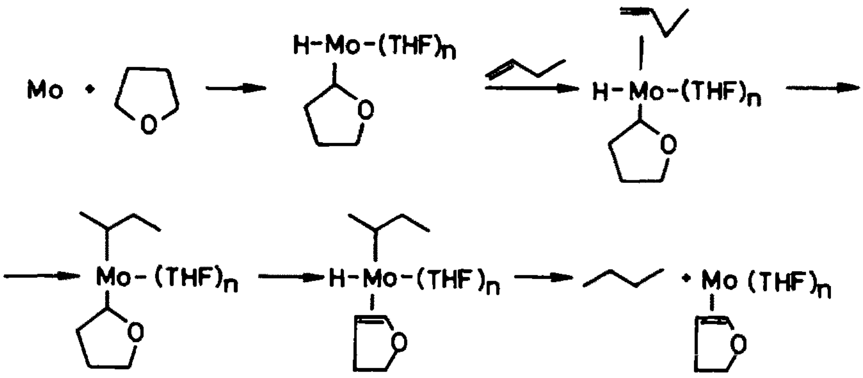
The reaction is quite general and does not affect many other reducible groups like $-NO_2$, $-CN$. α,β-Unsaturated acyl chlorides may be reduced to α,β-unsaturated aldehydes with very good selectivity if 1 mole Bu_3SnH is employed [252].

c) Low Valent Transition Metal Complexes

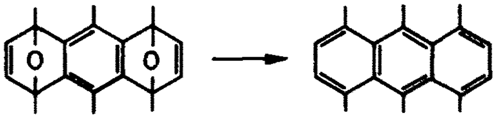
Nitroarenes are converted to aromatic amines using $Co_2(CO)_8$ on alumina. Probably the OH groups present on the surface of the oxide furnish the necessary H atoms [253]. $Mo(CO)_6$ on alumina and $Fe_3(CO)_{12}$ on alumina can be used to deoxygenate azoxy compounds to azo compounds and pyridine N-oxides to pyridines in 1,2-dimethoxyethane as solvent. The $Fe_3(CO)_{12}/Al_2O_3$ reagent is especially useful as it may be applied at room temperature and results in yields between 59-86% [254].

The reduction of N_2 with V(II)-pyrocatechol complexes occurs in a stepwise fashion with N_2H_2 and N_2H_4 as the intermediates. The high reduction potential of N_2 to N_2H_2 and the tendency of N_2H_2 to decompose into N_2 and H_2 are mainly responsible for the extreme dependence of the yields of NH_3 on pH and solvent (MeOH better than H_2O). The same system also reduces acetylenes to olefins, olefins (slowly) to alkanes, CO to CH_2O and CH_3OH, aldehydes to alcohols [255]. Cysteine was fixed onto an insoluble polymeric substrate via the carboxyl group to give the corresponding 1,2-aminethiol. The polymer supported Mo(VI)complex of the supported aminethiol reduced C_2H_2 to C_2H_4 [256].

When Mo atoms are cocondensed with THF at -196° and subsequently 1-butene is added to the matrix, hydrogenation of the alkene is observed. Several other alkenes as well as conjugated and cumulated dienes could be also reduced. The following mechanism has been proposed for this unusual hydrogenation [257]:

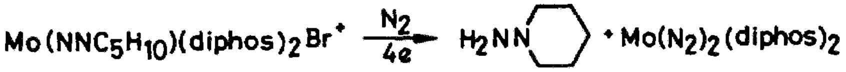


Low oxidation state complexes prepared from $TiCl_4$, VCl_3, $CrCl_3$, $MoOCl_3$, WCl_6 or $FeCl_3$ with Mg in THF react with $PhNO_2$ to give $PhNH_2$ and PhN=NPh and with PhN=NPh to give $PhNH_2$. $PhNH_2$ and PhN=NPh were formed via a nitrene mechanism [258]. Low-valent forms of Fe, W and Ti, produced by the treatment of $FeCl_3$, WCl_6 and $TiCl_3$ with BuLi at -78°, are useful deoxygenation catalysts for the conversion of arene-1,4-endoxides to the corresponding arenes in a single step [259]:



d) Organic Reductants in the Presence of Transition Metal Complexes

The C=C bond in α,β-unsaturated carbonyl compounds is quantitatively reduced by sodium formate in a two-phase system in the presence of $Ru(PPh_3)_3Cl_2$ as a catalyst and quaternary ammonium salts as phase transfer catalysts [260]. Nitrosobenzene is converted into azoxybenzene in the presence of $Ru(CO)_3(PPh_3)_2$ as catalyst at $80^{\circ}C$. In EtOH the reduction proceeds in an inert atmosphere. However, in toluene 10 atm CO has to be applied. At higher P_{CO}, azobenzene is the main product [261]. Carboxylic acids are reduced to aldehydes by iBuMgBr in the presence of catalytic amounts of $TiCp_2Cl_2$ in 48-73% yield [262]. Hydrolyzed particles of Mo(III) citrate complexes formed in the reduction of Mo(VI) or Mo(V) solutions in alkaline media (pH 10) on the Hg electrode possess catalytic activity for the electroreduction of acetonitrile. The main products of reduction are ethane, propane and propylene [263]. The Ru-Mo clusters $(bpy)_2RuS_2MoS_2$ and $[(bpy)_2RuS_2MoS_2Ru(bpy)_2](PF_6)_2$ were prepared and used as catalysts for the electrochemical reduction of acetylene in MeOH/DMF solution. Both ethylene and ethane were formed and also H_2 was evolved [264]. Electrochemical reduction of the Mo(IV) hydrazido complex (73) at a Pt electrode in THF - 0.2M $(NBu_4)(BF_4)$ under N_2 yields the free organohydrazine and the dinitrogen complex (74):



73

74

Since (74) is readily converted into (73) by 1,5-dibromopentane, a cycle for the fixation of N_2 as an organohydrazine is plausible [265].

Reduction of acetylene to ethylene is catalyzed by species formed in the controlled potential electrolysis of $Fe_4S_4(SPh)_4^{2-}$ and $Mo_2Fe_6S_9(SPh)_8^{3-}$ in MeOH/THF and in H_2O. The catalytic activity increased in the order $[Mo\text{-}Fe]^{4-} \ll [4\text{-}Fe]^{3-} \gg [Mo\text{-}Fe]^{5-} < [4\text{-}Fe]^{4-}$. In MeOD/THF various deuterated ethylenes were formed. The lack of stereoselectivity was probably due to the H-D exchange between acetylene and MeOD [266]. Ketones and acids derived from the $FeCp(\eta^6\text{-arene})^+$ complexes in which the function is attached to the ring are transformed into secondary alcohols or pinacols by cathodic reduction on Hg. The electroreduction is activated by the cationic organoiron group [267]. Several alkyl halides were reduced electrocatalytically on carbon cathodes modified with meso-tetra(p-aminophenyl)porphyrinatoiron(III). The electrodes show catalytic activity when the surface bound complex is reduced to formally Fe(I) [268].

The reduction of dibromoalkanes at electrodes to which Co(II)- or Cu(II)-tetra(p-aminophenyl)porphyrin were covalently attached was catalyzed by the metalloporphyrin [269].

IV. Oxidation

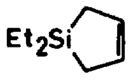
1. Catalytic Oxidations with O_2

a) Cr and Mo Catalysts

Kinetic data indicate that the catalytic effect of Cr(III)-carboxylates on the oxidation of pentadecane in $BuCO_2H$ is due to complexation of the Cr salt with $BuCO_2H$ [270].

$MoO_2(cys\text{-}OR)_2$ complexes (R = Me, Et, $PhCH_2$) have catalytic activity for the air oxidation of PPh_3. Reducing these complexes by PPh_3 at 25°C gives monomeric Mo(V) species showing ESR signals similar to those of reduced xanthine oxidase [271]. The kinetics of O-transfer from $MoO_2(cys\text{-}OEt)_2$ to PPh_3 and the reaction between $Mo_2O_3(cys\text{-}OEt)_4$ and O_2 in benzene solution have been investigated. The results are interpreted in terms of a bimolecular mechanism with the interaction of one $MoO_2(cys\text{-}OEt)_2$ and one PPh_3 molecule in the activated complex [272].

The catalytic activity of potassium cyanomolybdates in the 1-nonene oxidation by O_2 in liquid phase was studied at 60-80°. The catalysts remained as a heterogeneous phase in the reaction mixtures [273]. Oxidation of (75) by air in the presence of $VO_2(acac)_2$, $Mo(CO)_4py_2$, $Mo(CO)_6$ or Mo naphtenate gave mainly (76) and (77) [274].



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Irradiating $Mo^{V}O(TPP)OCH_3$ under air in a benzene solution containing 5% MeOH gave H_2O_2 [275]:

$$CH_3OH + O_2 \longrightarrow CH_2O + H_2O_2$$

The reaction is the result of a two step, photoassisted catalytic cycle:

$$Mo^{V}O(TPP)OCH_3 \xrightarrow{h\nu} Mo^{IV}O(TPP) + \cdot OCH_3(\rightarrow CH_2O)$$

$$2Mo^{IV}O(TPP) + O_2 + 2CH_3OH \longrightarrow 2Mo^{V}O(TPP)OCH_3 + H_2O_2$$

b) Mn Catalysts

The synergetic action of Mn and Na naphtenate catalysts in the oxidation of C_{12}-C_{17} n-alkanes was studied [276, 277]. The reaction rate in the oxidation of ethylbenzene with cobaltmanganese bromide catalyst to give PhCHMeOH, PhCOMe and PhCOOH depends on the concentration of Mn^{3+} and Br^- consistent with a nonchain radical mechanism [278].

The oxidation of ethylene in acetic acid to ethylene glycol mono- and diacetate was investigated with metal acetate + KI catalysts at 140° and 20 atm. KI + $Mn(OAc)_2$ was found to be the most reactive system. The slow step of the catalytic cycle is the reaction between HOI and C_2H_4 to form ICH_2CH_2OH. The $Mn(OAc)_2$ catalyzes the formation of HOI [278a]. Mn(TPP)Cl catalyzes the oxidation of olefins to ketones by air in the presence of $(NBu_4)(BH_4)$ in CH_2Cl_2 at room temperature. High concentrations of O_2 inhibit the oxidation. The ketones are partly reduced to alcohols by $(NBu_4)(BH_4)$ [279]. In the presence of colloidal Pt and H_2 Mn(TPP)Cl catalyzes the epoxidation of olefins by O_2. The role of the Pt is to catalyze electron transfer from H_2 to (TPP)Mn(III) to form (TPP)Mn(II) which activates O_2 [280].

Photoinitiated oxidation of PhCHO with O_2 is catalyzed by Mn(II)- or Cr(III)-ethylcapronate [281]. Chain initiation during the liquid-phase oxidation of 8-pentadecanone in the presence of $MnSt_2$ was first order in substrate, O_2 and $MnSt_2$ [282].

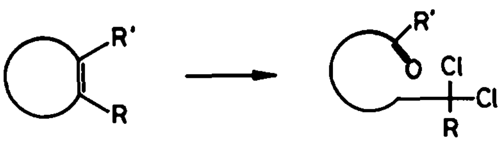
c) Fe, Ru and Os Catalysts

Olefins were oxidized in pyridine with O_2 in the presence of $FeCl_3$ under irradiation with Pyrex-filtered light [283, 284]. Mono and disubstituted olefins gave α-chloro ketones (eq. 1 and 2), while tri- and tetrasubstituted olefins gave dichloro ketones with a C-C bond cleavage (eq. 3 and 4)

$$C_6H_{13}CH{=}CH_2 \longrightarrow C_6H_{13}\overset{O}{\overset{\|}{C}}CH_2Cl$$

(eq. 1)

(eq. 2)



(eq. 3)

(eq. 4)

Oxidation of butyraldehyde with O_2 to butyric acid catalyzed by ferrocene was carried out at 35° in different solvents [285]. The rates of reaction of o- and p-substituted halophenylhydrazines with O_2 in the presence of Fe^{3+} and oxyhemoglobin were compared [286].

Ru(II) phosphine complexes like $Ru(PPh_3)_3Cl_2$ catalyzes the oxidation of allyl alcohols to α,β-unsaturated carbonyl compounds by O_2 at room temperature in 1,2-dichloroethane solution. Yields are generally high and the reaction proceeds with retention of stereochemistry. The PPh_3 ligand is rapidly oxidized to Ph_3PO. The mechanism of these catalytic oxidations probably involves formation of a Ru alkoxide [287]. Addition of acetonitrile to the traditional CCl_4/H_2O solvent mixture for RuO_4 catalyzed oxidations leads to a greatly improved and reliable system. Yields above 75% were achieved for the following transformations: oxidative cleavage of olefins to carboxylic acids, oxidation of primary alcohols to carboxylic acids and ethers to esters, and oxidative degradation of aromatic rings to carboxyl groups. The effect of acetonitrile is explained by its good ligating ability thereby preventing the formation of catalytically inactive lower valent Ru carboxylate complexes [288].

OsO_4 efficiently catalyzes the oxidation of olefins to glycols by O_2 in the presence of organic selenoxides as cooxidants. The cooxidant oxidizes soluble Os(VI) to Os(VIII):

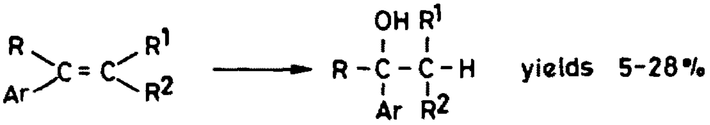
$$R_2SeO + OsO_4^{2-} + H_2O \longrightarrow R_2Se + OsO_4(OH)^{2-}$$

and the selenides can be reoxidized to selenoxides by photochemically generated singlet oxygen [289].

d) Co and Rh Catalysts

$CoSt_2$, $MnSt_2$ or $CrSt_3$ increased the rate of oxidation of pentadecane with O_2 at 120-140° catalyzed by $AlSt_3$ [290].

Oxidation of C_2H_4 by O_2 was studied in AcOH using $Co(OAc)_2$ + NaBr as catalyst. The major products after 24 at 165° were $AcOCH_2CH_2OAc$, $BrCH_2CH_2Br$ and CO_2. The results suggest that $BrCH_2CH_2Br$ is the main precursor of $AcOCH_2CH_2OAc$ [291]. The catalytic activity of polymeric complexes of first row transition metals in the low-temperature liquid-phase oxidation of α-olefins was greater for metals with an odd number of electrons. The most active complexes were those of Co^{2+}. Of polymeric ligands tested, the most active was polyvinyl alcohol [292]. Aryl-substituted olefins were converted to benzyl alcohols regioselectively by O_2 and BH_4^- in presence of Co(dmg)(py)Cl as catalyst [293]:



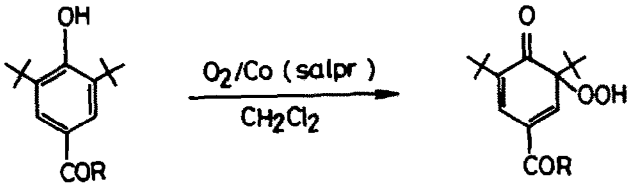
Co and Mo complexes were effective catalysts for the oxidation of α-methylstyrene [294].

Kinetic data for toluene oxidation in the presence of $Co(OAc)_2$ and NaBr were determined [295]. In the liquid-phase oxidation of methylbenzenes in AcOH at 150° using $Co(OAc)_2$ and $Cu(OAc)_2$ and NaBr catalyst the corresponding benzyl acetates and benzaldehydes were obtained in high selectivity [296]. The kinetics of oxidation of PhMe in the presence of Co(III) acetate was investigated in the presence of KOAc and dibenzo-18-crown-6 [297]. Added bpy increases the rate and decreases the activation energy of p-xylene oxidation with Co and Mn caprylate catalysts. It increases, however, also the extent of decarboxylation [298]. The oxidation of durene to pyromellitic acid by O_2 in the presence of Co(III) has been studied. In the absence of a strong acid pyromellitic acid is associated with Co as insoluble aggregates. In the presence of strong perhalogenated carboxylic acids durene is transformed into pyromellitic acid in an almost quantitative yield below 100° [299]. The oxidation of dichloro-1,2,4,5-tetramethylbenzene with $Co(OAc)_2$ + NaBr as catalyst involved organic bromide formation during chain initiation [300].

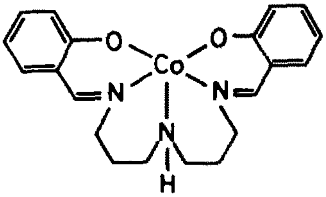
Several Co complexes on silicagel catalyzed the oxidation of tetralin to hydroperoxide, alcohol and ketone. The highest conversion was obtained with the bpy complex [301]. The highest yield of dicarboxylic acid in the oxidation of 2,6-dimethylnaphtalene with a Co^{2+} + Mn^{2+} + Ce^{3+} bromide catalyst was obtained at $(Co^{2+})/(Co^{2+})+(Mn^{2+})+(Ce^{3+})$ ratios of 0.125 - 0.87. Et_3N increased the reaction rate and the conversion to dicarboxylic acid [302].

In the presence of Lewis acids like $BF_3 \cdot Et_2O$ or $LiPF_6$ cobalt-nitro complexes such as pyCo(saloph)NO_2 or pyCo(TPP)NO_2 oxidize primary alcohols to aldehydes and secondary alcohols to ketones. As the nitrosyl complexes formed in this reaction may be reoxidized by O_2 in the presence of Lewis acids to the starting nitro complexes, a catalytic cycle is possible using O_2 as the oxidant [303]. The oxidation of iPrOH in AcOH catalyzed by solid and polymer-bound Co(II) complex ions was studied. In both cases the catalyst acts as an initiator of the decomposition of peroxides to radicals [304]. The rate of oxidation of saturated aldehydes with Co(III) acetylacetonate catalysts increased with the σ^* value of R in RCHO (R = iPr, Pr, Et, Me). Unsaturated aldehydes were oxidized more slowly than the saturated ones and no structure-reactivity relationship was observed [305]. Spectrophotometric investigations have been carried out for the systems $CoCl_2 \cdot 6H_2O$ + acrolein + O_2 and $CoCl_2 \cdot 6H_2O$ + peroxyacetic acid in acetone solutions. Based on the spectral similarities in the initial stages of the reaction it is postulated, that the decomposition of a peroxiacid - Co(III) complex is an important intermediate in the course of the oxidation of the aldehyde [306].

The oxidation of substituted phenols by O_2 and Co(II)-bis (3-(salicylideneamino)-propyl)methylamine as catalyst is first order in $[O_2]$, [substrate] and [Co]. The results indicate that metal-bound O_2 is an active species in the oxidation of phenol [307]. 4-Acyl-2,6-di-t-butylphenols were oxygenated in the presence of Co(salpr) (78) exclusively at the ortho position in 92-98% yield [308]:

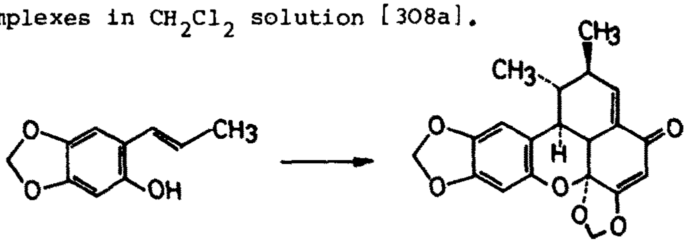


R = Me, iPr, tBu, Ph, OMe



78

Carpanon (80) was synthesized in 78-94% yield by the oxidation of (79) with O_2 in the presence of Co(II), Fe(II) or Mn(II) Schiff base complexes in CH_2Cl_2 solution [308a].



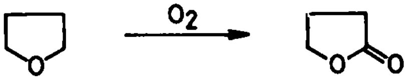
79 80

The oxidation of benzoin has been studied in detail with $Co(acac)_2$ as catalyst and MeCN as solvent. The rate determining step is probably the loss of a proton from a dimeric cobalt complex containing benzoin [309]. Dehydroabietic acid was oxidized with O_2 in the presence of $Co(acac)_2$ and Mn-2-aceto-δ-chlorovalerolactonate catalysts [310].

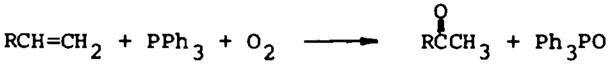
Oxygenation reactions of skatole catalyzed by Co(II) complexes are strongly retarded upon addition of a Lewis base such as pyridine [311]. Cobalt(II) complexes catalyze the oxidation of adrenaline [312].

Bifunctional catalysts composed of a polymeric base and a Co phthalocyanine were applied to the oxidation of thiols to disulfides by O_2. Hydrogen peroxide is produced and partly consumed during this reaction. The reaction of H_2O_2 with thiols results mainly in the formation of disulphides. However, small amounts of sulfur-containing oxyacids are also formed which poison the essential basic sites and thus deactivate the catalyst [313]. The kinetics of the oxidation of mercaptobenzthiazole to the corresponding disulfide was examined with sulfonated Co phtalocyanine catalysts at 40-50°. Amines decreased the rate [314]. First-order rate constants and activation parameters were determined for the oxidation of 2-benzothiazolethiol by O_2 with Co phthalocyanine-tetrasulfonate and some derivatives as catalysts. Electron-donating substituents increased the activity of the catalyst [315]. The oxidation rate of MSEt (M = Li, Na, K) by O_2 in the presence of Co disulphthalocyanine passed through a maximum with increasing MOH concentration [316]. Oxidation of acetylmethylthiophenes by O_2 with a $Co(OAc)_2$ + NaBr catalyst gave the corresponding acetylthiophenecarboxylic acids via aldehydes [317]. 2-Ethyl-3-methylthiophene yields mainly 3-methyl-2-acetyl-thiophene and 1-(3-methyl-2--thienyl)ethyl acetate. The kinetics of the reaction was determined [318].

Rh(I)-carbonyl complexes on an SH-functionalised silica gel support $[SG]\text{-}SRh(CO)_2(solv)_n$ ([SG] = silica gel treated with $(MeO)_3SiCH_2CH_2CH_2SH$; solvent = THF or EtOH) catalyze the oxidation of 1-hexene to 2-hexanone by O_2 in the presence of Cu(II). The catalyst activity increases as the surface sulfide concentration of the silica gel is decreased. Thus the dimer form $(\mu\text{-}[SG]\text{-}S)_2Rh_2(CO)_4$ is inactive. This supported catalyst is much less susceptible towards degredation than its homogeneous counterparts [319]. $[Rh_2(C_5Me_5)_2(OH)_3]Cl\cdot 4H_2O$ catalyzes the oxygenation of THF to γ-butyrolactone at 20°C in the presence of small amounts of water:



The same complex also catalyzes the oxygenation of Ph_3P to Ph_3PO [320]. The complexes $Rh(CN)(PPh_3)_3$, $Rh(OCN)(PPh_3)_3$ and $Rh(SCN)(PPh_3)$ are catalysts for the co-oxygenation of 1-octene and PPh_3 in benzene solution at 20-60°C:

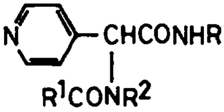


$$RCH{=}CH_2 + PPh_3 + O_2 \longrightarrow RC(=O)CH_3 + Ph_3PO$$

The catalytic oxygenation is less efficient with styrene as the olefinic substrate [321].

e) Ni, Pd and Pt Catalysts

The electron donors HMPA, N-methyl-2-pyrrolidone and DMF accelerated the Ni(acac)$_2$-catalyzed oxidation of PhEt and increased the selectivity for PhCHMeOOH [322]. Pyridylglicine derivatives (81)

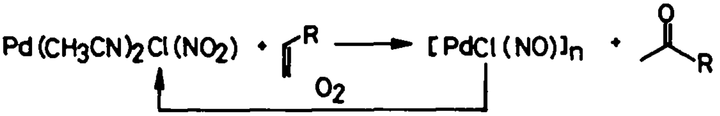


81

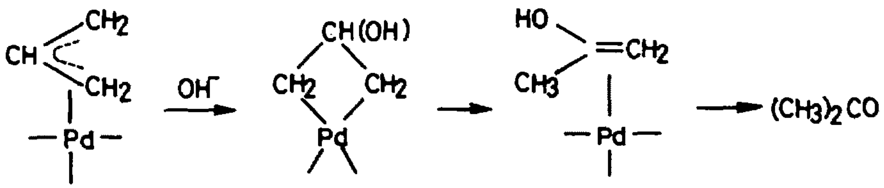
were cleaved by O_2 in the presence of Ni(II) phthalocyanine to give the corresponding peptides R^1CONHR^2 [323].

The $PdSO_4$ + $H_3PMo_6W_6O_{40}$ system is an effective catalyst for the oxidation of olefins to ketones. Oxidation of 1-octene at 60-80° gave 2-octanone with 95% selectivity [324]. In the case of cycloolefins H_2O/DMF is the most effect solvent mixture and cyclopentene the most reactive substrate [325]. MeCOEt was prepared by oxidation of 1-butene at 36° and pH 1.1-1.3. The $PdSO_4$ + $H_3PMo_6W_6O_{40}$ catalyst showed higher activity than the Wacker catalyst at pH<2.3 [326].

$Pd(CH_3CN)_2ClNO_2$ also catalyzes the oxidation of olefins to ketones. The catalytic cycle is based in this case on a nitro--nitrosyl redox couple:



If $Pd(CH_3CN)_2(NO_2)_2$ is used, 2-nitro-1-alkenes are formed as by-products [327]. Hexa-1,5-diene is catalytically converted into acetone in an aqueous solution of $Pd(PhCN)_2Cl_2$, $CuCl_2$ and CuCl at 60°C in the presence of O_2. A mechanism involving the formation of a (η^3-allyl)$_2$Pd(II) complex and the conversion of the η^3-allyl ligands into acetone has been suggested for this reaction:

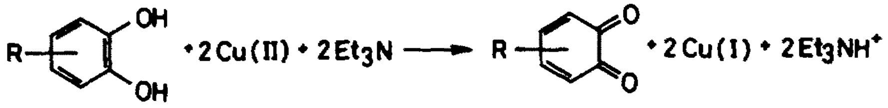


Possibly the Wacker-oxidation of propylene and higher alk-1-enes into ketones is also proceeds through η^3-allyl intermediates in contrast to the case of ethylene, where a π-bonded olefin is involved in the reaction with the OH^- ion [328].

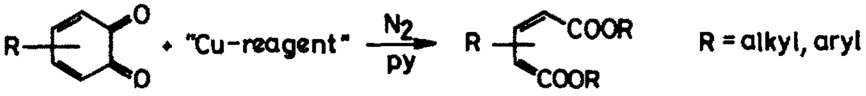
The catalytic oxidation of cyclohexanol is promoted by 18-crown-6-ether/K/Pd/acetate/chloride. The active catalyst involves ion-pair complexes [329]. PtO_2L_2 (L = PPh_3, PCy_3) complexes react with Ph_3CBr or PhCOBr to yield the corresponding dialkyl and diacyl peroxides $Ph_3COOCPh_3$ and PhCOOOCOPh. Alkyl- and acyl peroxo Pt(II) complexes $L_2PtBr(OOR)$ (R = CPh_3, COPh) were isolated as intermediates [330].

f) Cu Catalysts

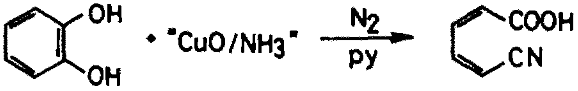
Detailed experimental results have been published [331] on the following, Cu(II)-induced oxidations of aromatic substrates:
a) catechols to o-quinones either stoichiometrically by $CuCl_2$ in the presence of Et_3N



or catalytically by O_2 in the presence of Cu(II) species produced by the reaction of O_2 with a solution of CuCl in CH_2Cl_2 containing py; b) o-benzoquinones or phenols to muconic acid monoesters with Cu(II) reagents prepared by the addition of alcohols or phenols to the products of oxidation of CuCl in py:



c) catechols, o-quinones (under N_2) and phenols (under O_2) to muconic acid mononitriles by the "CuO/NH_3" reagent prepared by the oxidation of CuCl in py followed by addition of NH_3:



Air oxidation of $3,4-(HO)_2C_6H_3Me$ in aqueous solutions of pH 6.5 was catalyzed by Cu(II) amine complexes [332].

The complexes [Cu(bpy)LI] (L = PPh_3, $PMePh_2$, PBu_3, PEt_3) react in DMF to form $[Cu_2(bpy)_2(OH)_2]I_2$; in the presence of a stoichiometric amount of base such as NaOEt they catalyze the oxidation of ethanol to acetaldehyde and H_2O_2:

$$C_2H_5OH + O_2 \longrightarrow CH_3CHO + H_2O_2$$

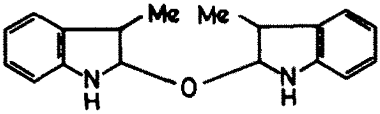
The catalytic decomposition of H_2O_2 by the complexes leads to their deactivation [333]. Bimetallic catalysts have been tested for the hydroxylation of anisole in the presence of a ligand and ascorbic acid. With catechol or dimethylglyoxime as a ligand (Cu^{2+} + Fe^{2+}) is an effective catalyst, but none of these metals alone is effective. The role of Cu is to catalyze the oxidation of ascorbic acid and in this way to furnish H_2O_2; the iron uses this peroxide to oxidize the anisole [334].

Oxidative cleavage of 3-substituted indoles (82) by O_2 is catalyzed by a CuCl + py complex in CH_2Cl_2:

82 58-81%

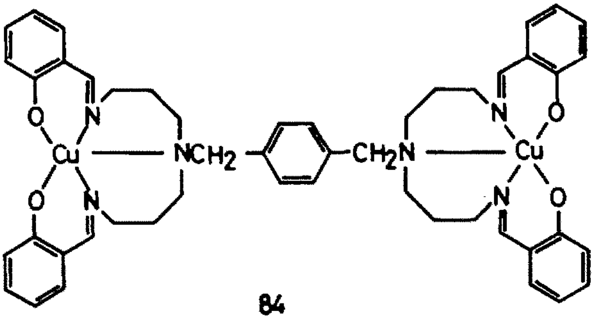
$R = Me, CH_2CH_2NHAc, CH_2COOMe, CH_2\underset{NHAc}{CH}COOMe$

Stoichiometric oxidation with Cu(II) compounds gave much lower yields and in the case of $Cu(OMe)_2$ or $CuCl_2 \cdot CuO$ (the oxidized form of the CuCl + py system) furnished no ring cleaved product but exclusively (83) [335].



83

The binuclear Cu(II) complex (84) catalyzes the oxidation of



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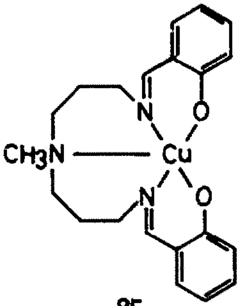

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N,N,N′,N′-tetramethyl-1,4-diaminobenzene by O_2 in a MeOH/DMF solution. The mononuclear complex (85) in inactive under the same conditions. This indicates that two adjacent Cu(II) ions of appropriate distance are necessary for the reaction [336].

The products of the copper catalyzed alkaline autoxidation of cysteine are cystine, H_2O and H_2O_2. No oxygen-containing sulfur acids are produced as long as cysteine is present. The reaction between H_2O_2 and cysteine is catalysed only by a Cu(I) complex. The Cu(II) complex present under autoxidation conditions is inactive in this respect [337]. ESR measurements indicate that $>98\%$ of the copper is present as Cu(II)-dicysteine complex. Based on kinetic data a reaction mechanism is proposed which involves thiyl- and superoxo-activated species as intermediates [338].

The oxidation of sulfides and sulfoxides with O_2 catalyzed by copper halides in acetone solution gave sulfoxides and sulfones in up to 100% yields. Second order rate constants were determined [339]. The Cu(I) complex Cu(phen)Cl reacts with O_2 at 20°C in methylene bromide to give $[Cu(phen)Cl]_2O$ in 95% yield. This complex oxidizes PPh_3 at 100°C in DMF with 100% yield (with respect to the oxygen):

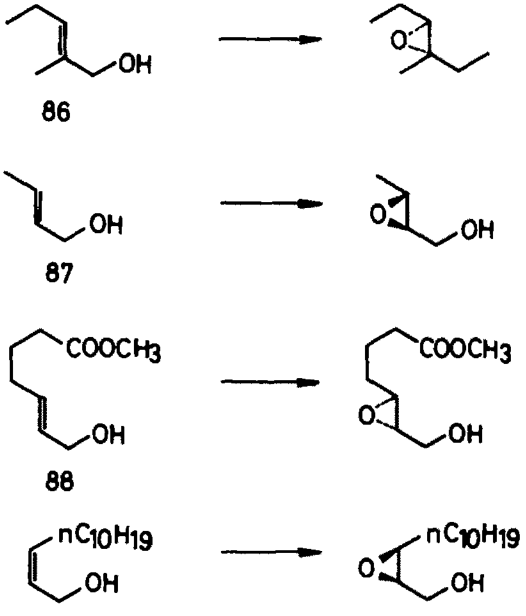
$$[Cu(phen)Cl]_2O + 3\ PPh_3 \longrightarrow OPPh_3 + 2\ Cu(phen)Cl(PPh_3)$$

This is the first example of a direct O-transfer to an organic substrate from an oxygenated copper complex [340].

2. Catalytic Oxidations Using Organic and Inorganic Oxidants

a) Ti Catalysts

Polymer-supported $TiCp_2Cl_2$ and $TiCpCl_3$ can be used as catalysts for the epoxidation of cyclohexene and cyclooctene by tBuOOH. The yields are low [341]. The allylic alcohols (86)-(89) could be epoxidized with >95% enantioselectivity by tBuOOH in the presence of (+) or (-) dialkyltartarates and $Ti(OPr^i)_4$ [342]:



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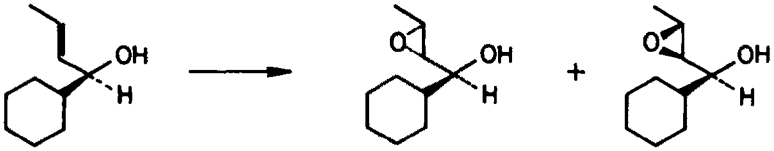
The $Ti(OPr^i)_4$ + diethyl-L-(+)-tartarate + tBuOOH reagent was used for the epoxidation of (90) to (91) [343]:

90

91

Racemic secondary allylic alcohols like (92) were diastereoselectively epoxidized (erythro:threo = 98:2) by tBuOOH with $Ti(OPr^i)_4$ as catalyst and in the presence of (+)-diisopropyl tartarate:

92



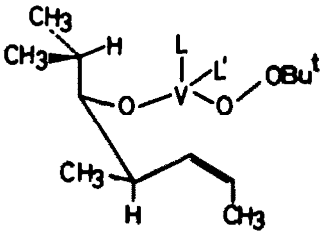
To achieve good enantiomeric purities an excess of tartarate ligand needs to be used. The enantiomeric purities of the unreacted allylic alcohols (at 55-60% conversion) are exceptionally high [344].

b) V Catalysts

The oxidation of phenol and substituted phenols using $KBrO_2$ in presence of vanadium(V) in binary solvent mixtures of acetic acid and water is first order with respect to oxidant and fractional with respect to substrate and catalyst [345]. The kinetics of the oxidation of cyclohexanone to adipic acid with $HClO_3$ catalyzed by vanadium(V) suggests that the rate determining step is the redox reaction

$$V^{5+} + C_6H_{10}O \longrightarrow V^{4+} + C_4H_8(COOH)_2$$

and that the vanadium(V) species is activated by $HClO_3$. This latter effect is also supported by the shift of light absorption of vanadium(V) solutions upon addition of $HClO_3$ [346]. The direction and degree of asymmetric induction observed during the V^{5+}/tBuOOH epoxidation of homo allylic alcohols could be explained by a vanadate ester transition state in which the metal is tetrahedrally coordinated, e.g. (93) [347]:



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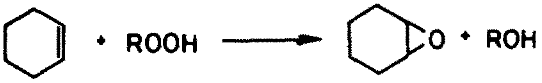
c) Mo and W Catalysts

The epoxidation of propylene by tBuOOH in tBuOH was catalyzed by Mo carboxylates and Mo + tBuOOH, MoO_3 + tBuOOH or MoO_4 + tBuOOH complexes [348]. The formation of propylene oxide with PhCHMeOOH and Mo naphtenate catalyst was not affected at 60-120° by radical scavengers like ionol, by the PhCHMeOH or the initial PhCHMeOOH concentration, or by the temperature [349].
$H_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]\cdot 4H_2O\cdot Me_2CO$ catalyzes the epoxidation of cyclohexene by cumene hydroperoxide (ROOH):



NMR measurements have shown that the first stage of the reaction is the formation of an intermediate complex between the Mo(V) compound and ROOH [350]. [MoO(TPP)X] (X = Cl, OMe) complexes catalyze the selective epoxidation of olefins with tBuOOH. Spectral evidence supports $MoO(TPP)OOBu^t$ as an intermediate of the catalytic cycle; the olefin probably reacts without coordination to the metal center [351]. Epoxidation and allylic oxidation of cholesteryl acetate with tBuOOH were studied in the presence of Mo complexes. Similar results were obtained in the presence of $MoO_2(acac)_2$, $Mo(CO)_6$ or $MoCl_5$ [352].

The double bond of silyl enol ethers is cleaved by tBuOOH in the presence of $MoO_2(acac)_2$ as catalyst to give carbonyl compounds:

The yields are almost quantitative [353].

"Molybdenum peroxide" and MoO_3 catalyze the oxidation of secondary alcohols to ketones by DMSO in toluene at reflux temperature [354]. The oxidation of several phenyl substituted arylmethyl sulfides, p-chlorophenylmethylsulfoxide and 1-methylcyclohexene with H_2O_2 in the presence of $MoO_2(acac)_2$, $Mo(CO)_6$ or $MoO_6\cdot HMPA\cdot H_2O$ has been studied in EtOH. The reactions afford the corresponding sulfoxides, the sulfone and the epoxide, respectively, in quantitative yields. The reactivity order is sulfide > sulfoxide > alkene. The oxidizing agent formed in solution is suggested to be the peroxo complex $MoO_5(EtOH)_2$ [355].

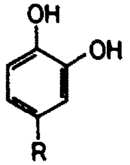
The catalytic oxidation of monohydric phenols by H_2O_2 in the presence of H_2WO_4, $NaHWO_4$ or $(NH_4)HWO_4$ at 80° proceeds by an electrophilic mechanism via a HWO_5 intermediate which forms a complex with phenol. The phenols undergo hydroxylation in ortho position [356]. The catalytic oxidation of ethylguaiacylcarbinol (a lignin model compound) by H_2O_2 in the presence of H_2WO_4 at 30° is a first order reaction with respect to ethylguaiacylcarbinol and H_2WO_4 and a zero order one with respect to H_2O_2 [357]. The oxidation of DMSO by H_2O_2 in the presence of Na_2WO_4 catalyst has been studied kinetically [358].

d) Fe, Ru and Os Catalysts

Catalytic oxidations like (eq.5), involving transition metal cations and their oxides in the gas phase, were observed by ion cyclotron resonance spectroscopy [359]:

$$C_2H_4 + 2\,N_2O \xrightarrow{Fe^+ \text{ or } FeO^+} 2\,N_2 + CO + CH_2O \qquad \text{(eq.5)}$$

Benzene was hydroxylated with H_2O_2 in a benzene + water two-phase system in the presence of Fe^{3+} and a variety of catechols (94) as ligands:



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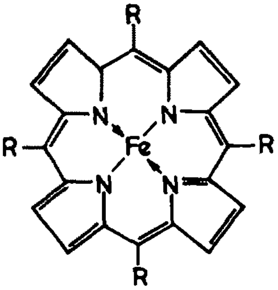
The hydrophobic catechols (R = nBu, n-C_6H_{13}, $PhCH_2$ and $PhCH_2CH_2$) did yield more effective catalyst than the water-soluble ones (R = Me, Et) [360].

The water-soluble iron porphyrin complex (95)



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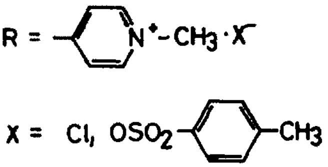
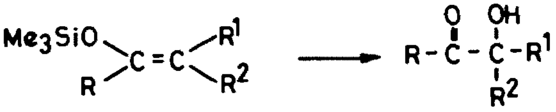


catalyzes the hydroxylation of phenylalanine by aqueous H_2O_2 to generate tyrosine and dihydroxyphenylalanine (DOPA) in about 70% yield. Complex (95) is a superior catalyst for this reaction in comparison with $FeCl_3$ [361].

The Ru(IV)-catalyzed oxidation of alkanes in aqueous solutions involves activation of the oxidant [Cr(VI), HNO_3, $HClO_4$ etc.] via Ru(IV) complex formation and is accompanied by H atom abstraction from the alkane by the activated oxidant [362]. A spectrophotometric study of the $RuCl_3$ catalyzed oxidation of alcohols by bis tellurato cuprate(III) showed that the reaction is zero order in Cu(III) and first order in Ru(III) and alcohol [363]. $Ru(PPh_3)_3Cl_2$ catalyzes the oxidation of alcohols by iodosylbenzene to aldehydes, ketones or acids. Primary aliphatic alcohols are transformed to carboxylic acids with excess iodosylbenzene, the reaction can be stopped at the aldehyde stage if phenylidosodiacetate is used as oxidant [364]. The Ru(III)-catalyzed oxidation of glycolate, lactate, and mandelate ions by hexacyanoferrate is approximately zero order in $Fe(CN)_6^{3-}$ and first order in Ru(III) [365]. The catalytic activity of $Ru(NO)(NO_3)_2.2H_2O$, and K[Ru(LH)Cl] (LH_4 = EDTA) in p-benzoquinone oxidation by Mn^{3+} is 1-2 orders of magnitude lower than that of Ru sulfate complexes [366].

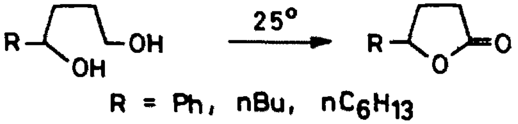
Silyl enol ethers (which can be derived from ketones) are oxidized by OsO_4 as catalyst and N-methylmorpholine-N-oxide monohydrate as stoichiometric oxidant to α-ketols in good to excellent yields [367]:



The kinetics of the OsO_4-catalyzed oxidation of $MeCHBrCO_2H$ with $Fe(CN)_6^{3-}$ was determined in aqueous alkali [368].

e) Ni and Pd Catalysts

Primary, secondary 1,4-diols were oxidized with good yields to lactones with Br_2 in the presence of Ni(II)-2-ethylhexanoate [369]:



Ethylene oxidation in solutions containing $PdSO_4$ and $KBrO_3$ gives mainly CH_3CHO and $BrCH_2CH_2OH$ in a 2:1 ratio. During the induction period Br_2 is formed, and this catalyzes the reoxidation of Pd^0 to Pd^{2+} [370]. Alcohols are oxidized to carbonyl compounds with CCl_4 in the presence of bases and $Pd(OAc)_2$ or $PdCl_2$ as catalysts. Yields are 35-75% [371]:

$$R_2CHOH + CCl_4 + \text{base} \xrightarrow[80-120^{\circ}C]{[Pd]} R_2C{=}O + CHCl_3 + HCl.\text{base}$$

$Pd(OAc)_2$ in the presence of 2 equivalents of PPh_3 catalyzes the oxidation of unsaturated alcohols to the corresponding ketones by bromobenzene or bromomesitylene as oxidants at 50°C. One mole of base (NaH or K_2CO_3) per mol of alcohol has to be added to prevent the formation of arylketones as coupling products [372].

f) Cu and Ag Catalysts

Benzylic hydrocarbons (e.g. alkylbenzenes and tetralin) were oxidized to aldehydes and ketones by Cu^{2+} + $S_2O_8^{2-}$ in aqueous MeCN or aqueous HOAc [373]. A mechanism has been proposed for the Cu(II)-catalyzed oxidation of maleic acid by the peroxydisulfate ion [374]. The oxidation of maleic acid in the presence and absence of Cu(II) by Cr(VI) in H_2SO_4 was studied. Two intermediates, mesotartaric acid by 2-electron abstraction and formyl hydroxy acetic acid by 4-electron abstraction could be isolated [375]. Aqueous potassium peroxydiphosphate brings about aromatic ring hydroxylation of benzene and toluene in modest yields in the presence of Cu^{2+}. Selectivity increases with decreasing acidity and with increasing concentration of Cu^{2+} [376].

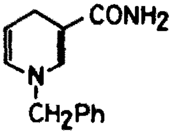
The oxidation kinetics of dl-atrolactic, benzilic, mandelic, and α-hydroxyisobutyric acid by $S_2O_8^{2-}$ in the presence of Ag(I) have been determined. Various metals inhibit the reaction [377]. $R(CH_2)_3CR^1(OH)CN$ (R = H, alkyl; R^1 = Me, Bu) were oxidized by $Ag^+ + S_2O_8^{2-}$ to give $RCH(CN)CH_2CH_2COR^1$. The oxidation involved alkoxy radical formation followed by migrations of H and CN [378].

g) Miscellaneous

The nuclear magnetic relaxation titration method was applied to study the oxidation of malonic acid with BrO_3^- in the presence of Mn^{3+}/Mn^{2+} as catalyst. Thereby, the oscillating nature of the reaction could be followed conveniently [379].

Anthracene is oxidized to anthraquinone by tBuOOH in 96% yield in the presence of $Rh(PPh_3)_3Cl$ as catalyst in benzene solution at 70°C. The same reagent effects epoxidation of olefins too, but the selectivity of this reaction is much lower [380].

The kinetics of the oxidation of (96) by $Fe(CN)_6^{3-}$ in the presence of different metal ions was investigated [381].



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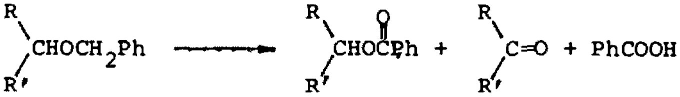
The catalytic activities of the compounds $M_3O(OOCR)_6(H_2O)_3^{n+1}$ (M = V, Cr, Mn, Co, Ru, Rh, Mo) attached to a Wofatit-type ion exchange resin have been compared for the epoxidation of cyclohexene with cumene hydroperoxide [382].

3. Stoichiometric Oxidations with High Valent Transition Metal Complexes

a) Cr and Mo Complexes

The kinetics of oxidation of iPrOH and 1-butoxy-2-propanol by pyridiniumchlorochromate catalyzed by $CHCl_2COOH$ or CCl_3COOH has been investigated in PhCl and $PhNO_2$ mixtures. A mechanism is proposed [383]. Chromium complexes supported on various polyvinylpyridine resins were used to oxidize 2-octanol to 2-octanone selectively [384]. The rate constans for the photon-activated oxidation of aliphatic alcohols by $HCrO_4^-$ obeys a linear free-energy relationship with Taft constants that suggest a 2-electron-transfer rate-determining step [385]. Benzyl ethers of secondary alcohols are oxidized by Jones reagent (CrO_3 in sulfuric acid) in acetone solution to benzoate esters and ketones:



Accordingly, the benzyl group may not be used to protect alcohols under such conditions [386].

The kinetics of picolinic acid-catalyzed oxidation of cyclohexanone by chromic acid in H_2O showed a change from first to zero-order dependence on cyclohexanone as well as H^+ [387]. The reaction between ascorbic acid and Cr(VI) in acid media is first order with respect to both reactants [388]. The oxidation of steroidal π-allylpalladium chloride complexes with Cr(VI) oxide in DMF containing ether to dissolve the complex and a trace of H_2SO_4 afforded the corresponding α,β-unsaturated ketones [389].

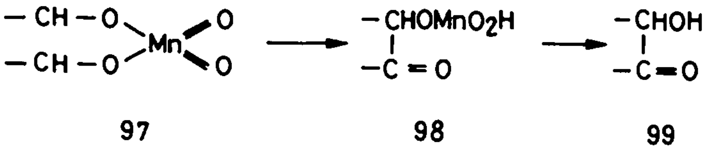
The kinetics of oxidation of Me_2S, Pr_2S and Ph_2S by pyridinium chlorochromate in chlorbenzene + nitrobenzene mixtures show Michaelis-Menten behavior. The oxidation is catalyzed by organic acids [390]. The kinetics of chromic acid oxidation of serine, methionine and cysteine is solutions containing $HClO_4$ were first order in chromic acid, amino acid, and H^+. $CoCl_2$ accelerated the rate [391].

Crotonaldehyde is oxidized to furan by $H_3PMo_{12}O_{40}$ (12-molybdophosphoric acid); this reaction is enhanced by water [392].

b) Mn Complexes

The preferential rupture of the C(α)-C(β) bond in $EtCO_2^-$ with MnO_4^- in highly concentrated NaOH was confirmed [393]. The oxidation of oxalate by permanganate exhibits kinetic bistability [394].

The oxidation of (E)-5-decene by $KMnO_4$ in slightly acidic aqueous Me_2CO gives 5-hydroxy-6-decanone as the initially formed product [395]. The D-labeled symmetrical olefins ethylene 1,1-d_2 and cyclohexene-1-d were oxidized by $KMnO_4$ and the D distribution in the products determined. The results suggest, that the intermediate cyclic manganate ester (97) first undergoes oxidative decomposition to (98) which is hydrolyzed to the α -ketol (99) [396]:

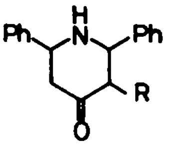


Indirect evidence was presented for the presence of a transient penta- or hexacoordinated species during the permanganate oxidation of 1,5-hexadiene [397]:

Solid $KMnO_4 \cdot H_2O$ is an efficient and selective agent for the oxidation of primary alcohols and aldehydes to carboxylic acids, secondary alcohols to ketones, dialkyl sulfides to sulfones and primary alkylamines to nitro compounds [398]. $KMnO_4$ adsorbed on solid supports (bentonite or $CuSO_4$) can be used to oxidize unsaturated secondary alcohols to the corresponding ketones in refluxing CH_2Cl_2 without degradation of the C=C bonds [399]. Benzyl(triethyl)ammonium permanganate oxidizes primary alcohols to carboxylic acids (or in CH_2Cl_2 as solvent to methylene dicarboxylates), secondary alcohols to ketones, primary and secondary amines to nitriles and amides, tertiary amines selectively to N,N-dialkylamides [400]. The rate of oxidation of benzhydrol to benzophenone by alkaline permanganate is only slightly influenced by pressure between 1 and 1000 atm. This supports a H atom transfer in the rate-determining step [401]. Kinetic data of the acid-catalyzed oxidation of tartaric acid with MnO_4^- in H_2SO_4 indicate the proton abstraction by the H_2O molecule to be rate-determining [402]. The oxidation of tartaric acid, malic acid, cyclohexanol, and allyl alcohol by $Mn(SO_4)_3$ shown first or second order kinetics at low and high concentrations of Mn(III) respectively [403].

Oxidation of ergosterol acetate and of 7-dehydrocholesterol acetate by $KMnO_4$ in H_2O-cyclohexane was investigated [404]. The kinetics and mechanism of oxidation of a few 1,2- and 1,4-dihydroxybenzenes to the corresponding o- or p-quinones by ethylenediaminetetraacetato-manganate(III) has been investigated by the stopped-flow technique. The interaction between Mn(III) and these substrates involves, as its rate determining step, the first electron abstraction to give the semiquinone radical [405].

The kinetics of oxidation of DL-proline by Mn(III) sulfate in acidic media is first order in DL-proline and Mn(III) and inverse first order in H^+ [406]. The oxidative splitting of the triacetoneamine heterocycle by $KMnO_4$ resulted in 35% $HOOCCMe_2NHCMe_2CH_2COOH$ [407]. Oxidation of N,N-dialkyladenosine derivatives with $KMnO_4$ in 50% AcOH gave both the mono- and di-dealkyl derivatives [408]. Oxidation of piperidones (100) with acidic-aqueous $KMnO_4$ was first order each in the oxidant, substrate and H^+ [409]. The permanganate ion oxidation of uracil (101) and



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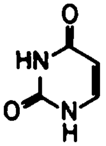
R = H, Me, Me_2CH



101

its 5-substituted derivatives is first order in each reactant. The initial oxidation step probably involves a concerted [3+2] cycloaddition step of MnO_4^- across the 5,6 double bond of the uracil. After this a soluble Mn(IV) species is formed (probably H_2MnO_3) which slowly precipitates [410].

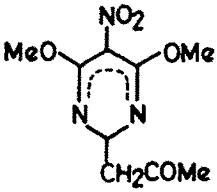
$[(PhCH_2)Et_3N](MnO_4)$ oxidized sulfides or sulfoxides in CH_2Cl_2+ AcOH at -10° to give the corresponding sulfones in 63-98% yield [411].

c) Fe, Ru and Os Complexes

Irradiation of primary alcohol (RCH_2OH) solutions of $Fe(ClO_4)_3$ with Pyrex-filtered light leads to a variety of products: RCHO, CH_2O, RH, RR, RCH_2OR, alkenes and tetrahydrofurans; Fe^{3+} is completely reduced to Fe^{2+}. The primary process of this photooxidation is assumed to be alkoxy radical formation [412]:

$$RCH_2OH{\cdot}Fe^{3+} \xrightarrow{h\nu} RCH_2O{\cdot} + H^+ + Fe^{2+}$$

The kinetics and mechanism of alkaline $K_3[Fe(CN)_6]$ oxidation of morpholine has been studied. The rate-determining step is interaction of the morpholine anions with $Fe(CN)_6^{3-}$ to give a radical [413]. The kinetics of the oxidation of phenylhydrazine with $K_3[Fe(CN)_6]$ was studied in $HClO_4$ [414]. Oxidation of (102) with $FeCl_3$ gave (103) [415].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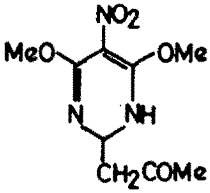
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Ruthenate oxidizes PhCHO, perruthenate both PhCHO and $PhCH_2OH$ to benzoic acid [416]. The oxidation of PPh_3 by $RuO^{2+}(bpy)_2(py)$ has been studied in MeCN solution. Kinetic and spectroscopic evidence supports the following mechanism [417]:

$$\mathrm{RuO(bpy)_2(py)^{2+} + PPh_3 \longrightarrow (RuO{=}PPh_3)(bpy)_2(py)^{2+}}$$

$$\xrightarrow[\mathrm{slow}]{\mathrm{MeCN}} \mathrm{Ru(NCMe)(bpy)_2(py)^{2+} + Ph_3PO}$$

Oxidation of ethylene glycol by OsO_4 showed first order kinetics in both reactants [418].

d) Cu, Ag and Au Complexes

Electronic spectral and ESR data indicate that $CuCl_2$ oxidation of $PhNEt_2$, $PhNMe_2$, and p-$Me_2NC_6H_4NMe_2$-p initially produces the cation radicals of the amines [419].

The kinetics of the following reactions were investigated: oxidation of EtOH, iPrOH, $PhCH_2OH$ and glycolic and lactic acids with diperiodatoargentate(III) in alkaline medium [420], oxidation of acetone and MeEt, MePr, Me-iPr and Me-tBu ketones by ditelluratoargentate(III) in alkaline medium [421] and oxidation of DMF and N-methylformamide by Ag(II) [422].

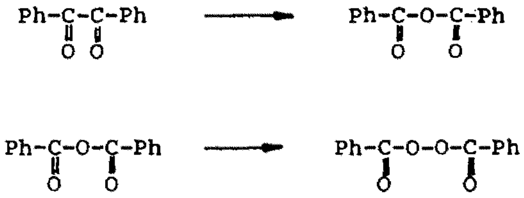
The disulfide bonds in proteins and peptides (e.g.insulin) are oxidatively cleaved by AuX_4^- (X = Cl, Br) to sulphonic acids. This rapid and irreversible process results in denaturation of the protein and may be a principal contribution to the toxicity of gold(III) [423].

e) Miscellaneous

The kinetics of the oxidation reaction of D-sorbitol in sulfuric acid medium with vanadium(V) was determined [424]. The oxidation of butan-2-one by vanadium(V) in aqueous media showed first order kinetics each in 2-butanone and oxidant. The solvent D isotope effect suggested involvment of the enolic from of the ketone in a reaction occuring through free radical intermediates [425].

Allylic oxidation of various olefins (allylbenzene, oct-1-ene, trans-oct-4-ene, C_5-C_8 cycloalkenes, 1- and 4-methylcyclohexene) with Co(III) acetate in acetic acid under N_2 gave exclusively the allylic acetate as the primary product [426]. The effect of H_2O on the oxidation of toluene by Co(III)acetate has been studied [427].

$PtO_2(Ph_3P)_2$ reacts with benzil or benzoic anhydride to yield benzoic anhydride or benzoyl peroxide, respectively [428]:



4. Electrooxidations

Depositing thin polymeric films containing the $(bpy)_2(H_2O)Ru(II)$ group bound to poly-4-vinylpyridine onto electrodes and oxidizing to Ru(IV) on the surface, catalytic oxidation currents were observed in the presence of iPrOH, p-toluic acid and the xylenes [429]. Graphite electrodes were modified by adsorption of cobalt phtalocyaninetetrasulfonate and used in a voltametric study of the anodic oxidation of cysteine. The electrocatalytic effect of the cobalt complex was shown [430]. The electrooxidation of aniline to benzoquinone was studied in the presence of Mn ions [431].

V. Reviews

Theoretical study of a homogeneous catalytic reaction: the $Rh(PPh_3)_3Cl$ catalyzed hydrogenation of olefins. 60 ref. [432]

Substrates and phosphorus ligands used in asymmetric homogeneous hydrogenations catalyzed by rhodium complexes. 116 ref. [434]

Asymmetric catalytic hydrogenation. 30 ref. [435]

Mechanistic aspects of homogeneous catalytic hydrogenation and related processes. 37 ref. [436]

Homogeneous catalytic reduction of carbonyl-, azomethine- and nitro groups. 68 ref. [437]

Synthesis of optically active compounds utilizing as catalysts transition metal complexes containing chiral P ligands. 265 ref. [438]

Asymmetric homogeneous catalysis by Ru complexes. 93 ref. [439]

Carbon monoxide activation: recent advances and developments in hydroformylation. Part III. 216 ref. [440]

Tetracarbonylhydrocobalt, the quintessential catalyst. 54 ref. [441]

The catalytic hydrogenation of carbon monoxide. The formation of C_1 compounds. 32 ref. [442]

A technological perspective for catalytic processes based on synthesis gas. 58 ref. [443]

Activation and stoichiometric reduction of CO. 26 ref. [444]

Experimental and theoretical studies of mechanisms in the homogeneous catalytic activation of CO. 30 ref. [445]

Activation of CO by C and O coordination. Lewis acid and proton induced reduction of CO. 45 ref. [446]

Oxidation of CO by metal ions and homogeneous catalysis of the water gas shift reaction and related processes. 42 ref. [447]

The importance of reactions of O bases with metal carbonyl derivatives in catalysis. Homogeneous catalysis of the water gas shift reaction. 29 ref. [448]

Homogeneous catalysis of the water gas shift reaction using simple mononuclear carbonyls. 22 ref. [449]

The water gas shift reaction: homogeneous catalysis by Ru and other metal carbonyls. 50 ref. [450]

The water gas shift reaction as catalyzed by Ru carbonyls in acidic solutions. 28 ref. [451]

Acetic acid by oxidation of C_4 hydrocarbons. 72 ref. [452]

Oxidation of alkylaromatic hydrocarbons with transition metal salts. 204 ref. [453]

The catalytic epoxidation of olefins with organic hydroperoxides. 197 ref. [454]

Metal-catalyzed epoxidations of olefins with hydroperoxides. 240 ref. [455]

Molecular metal clusters as catalysts. 50 ref. [456]

Novel industrial catalysts: supported organometallic cluster compounds. 161 ref. [457]

Immobilized transition metal carbonyls and related catalysts. 308 ref. [458]

Anchored complexes in fundamental catalytic research. 54 ref. [459]

Homogeneous or heterogeneous catalysis? 29 ref. [460]

Commercial applications of reactions catalyzed by soluble complexes of Co and Rh. 12 ref. [461]

Transition metal complexes as catalysts in biochemical systems. Interaction with electron transfer processes. 38 ref. [462]

Kinetics and mechanisms of redox reactions of transition metal complexes with organic substrates. 77 ref. [463]

Selective reactions of transition metals and their complexes. 31 ref. [464]

List of Abbreviations

Ac = CH_3CO
acacH = acetylacetone
ampy = 2-aminopyridine
bpy = 2,2'-bipyridine
COD = 1,5-cyclooctadiene
COT = cyclooctatetraene
Cp = η^5-cyclopentadienyl
Cy = cyclohexyl
cysH = cysteine
diglyme = (2-methoxyethyl)ether
diphos = 1,2-bis(diphenylphosphino)ethane
DMF = dimethyl formamide
dmg = dimethylglyoximato
DMSO = dimethyl sulfoxide
dmp = sodium diphenylphosphinobenzene-m-sulphonate
EDTA = ethylene diamine tetraacetic acid
HMPA = hexamethylphosphoric triamide
men = (R)-(-)-menthyl
nmen = (S)-(+)-neomenthyl
phen = 1,10-phenanthroline
salen = N,N'.bis(salicylidene)-ethylenediamino
saloph = N,N'-bis(salicylidene)-O-phenylendiamino
SG = silica gel

SIL = silica
solv = solvent
st = stearate, $nC_{17}H_{35}COO$
tol = tolyl
TPP = 5,10,15,20-tetraphenylporphinato
Ts = p-tolylsulfonyl

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