# TRANSITION METALS IN ORGANIC SYNTHESIS: HYDROFORMYLATION, REDUCTION AND OXIDATION

## ANNUAL SURVEY COVERING THE YEAR 1982

LÁSZLÓ MARKÓ

Department of Organic Chemistry, University of Veszprém,
H-8200 Veszprém, Hungary

CONTENTS

## Introduction

The papers in this survey 1982 have been largely grouped by reaction type and not by the transition metal complexes used in the organic transformations as it has been done for the survey 1981. The rearrangement of the material according to organic reactions has been performed because it was felt that such a grouping would make its presentation more clear. In order to aid those chemists, however, who are mainly interested in the transformations taking place within the coordination sphere of the metal an additional index has been compiled which enables the identification of all papers dealing with a special transition metal.

## I. Theoretical Calculations

Theoretical calculations and reinterpretations of literature experimental data suggest that hydrocarbyne complexes ($M\equiv C\text{-}OH$) may be important intermediates in homogeneous transition metal-catalyzed CO reduction [1]. Extended Hückel theory calculations have been carried out to investigate the possible formation of σ and π complexes between olefins and iron carbonyl hydrides, postulated as intermediates in hydroformylation of olefins with CO and $H_2O$ (Reppe synthesis) [2].

Nonempirical pseudopotential calculations were performed for $HPd(C_2H_4)Cl_3$. A collapse mechanism for the formation of planar $EtPdCl_3$ was proposed [3].

MO calculations for complexes formed in pyrocatechol + $Cu^{2+}$ + $O_2$ + $H_2O$ systems indicated that $O_2$ is not coordinated to $Cu^{2+}$ unless $H_2O$ is present in the coordination sphere [4]. The results of a mechanistic study using ab initio theoretical methods were used to outline plausible mechanistic sequences for alkane, alcohol and alkene oxidation by $CrO_2Cl_2$ and $MoO_2Cl_2$. It is suggested that the second oxo group is intimately involved in the reaction sequence [5].

## II, Hydroformylation and Related Reactions of CO

### 1. Hydrogenation of CO to Hydrocarbons and Oxygen-containing Organic Compounds [6-10]

In the synthesis of hydrocarbons and alcohols through hydrocondensation of CO, the complexes of Rh, Ru and Co were found to be the most active. With Ru catalysts the use of very high pressures (>3000 bar) leads to the synthesis of saturated long-chain alcohols ($C_1$ to $C_9$) according to a Schultz-Flory distribution [6]. The hydrogenation of CO to compounds containing MeO and $-OCH_2CH_2O-$ groups catalyzed by $Co_2(CO)_8$ or $Ru_3(CO)_{12}$ is significantly accelerated if the reaction is carried out in tri-n-hexylsilane as solvent (270°C, 200-600 bar). With $Ru_3(CO)_{12}$ as catalyst a desilylative reductive decarbonylation can also be observed [7]:

$$R_3SiH + CO + H_2 \longrightarrow RCH_2O-$$

Ethylene glycol mono- and diacetate, methyl- and ethyl acetate are formed from synthesis gas in the presence of homogeneous Ru catalyst at 220°C and 430 bar ($H_2/CO = 1/1$) in AcOH as solvent. Yields and selectivity to glycol esters are substantially improved through the addition of bulky cationic promoters, particularly $R_4P^+$ and $Cs^+$ [8]. $^{14}C$-Tracer studies show that MeOH and ethylene glycol are primary products of the homogeneous Rh-catalyzed conversion of CO + $H_2$ and do not undergo secondary transformation under the reaction conditions (220°C, 850 bar). Paraformaldehyde is readily converted into the typical mixture of reaction products most plausibly via a common reaction intermediate [9]. Ethylene glycol was detected in the products of reduction of CO by using combinations of $[H_3Mo(PMePh_2)_3]^+$ or $[H_5W(PMePh_2)]^+$ with $[Rh_{12}(CO)_{34}]^{2-}$ or $Co(CO)_4^-$ under a synthesis gas atmosphere at 5-100 bar and 25-200°C [10].

## 2. Hydroformylation

### a) Co Catalysts

Hydroformylation of alkenes over $Co_2(CO)_8$ and $Co_4(CO)_{12}$ at 1 bar and 100 bar CO pressure was studied. The kinetic parameters suggested both dissociative and associative mechanisms [11]. Hydroformylation of cyclohexene by $Co(acac)_2(H_2O)_2$ in benzene solution produced the corresponding aldehyde, alcohol and saturated hydrocarbon. A green complex $Co(acac)_2(C_6H_{10})$ has been isolated and shown to have a catalytic activity comparable to that of $Co(acac)_2(H_2O)_2$ [12]. In the hydroformylation of polypropylene oil with synthesis gas at 150-170°C in the presence of $Co_2(CO)_8$ catalyst, the reaction occured predominantly at the double bond in $-CH{=}CHCH_3$ groups, whereas the double bond in -CH=C(Me)- groups was not reactive. The reaction rate and conversion decreased and no alcohols were formed in the presence of $Rh(CO)(PPh_3)_2Cl$ [13].

The reactivity ratio of 1-, (EZ)-2-, (E)-3-, (E)-4-, (E)-5-, and (E)-6-dodecene toward hydroformylation at 120°C was 6:2:1:1:1:1 with $Co_2(CO)_8$ and 15:1:1:1:1:1 with $HRh(CO)(PPh_3)_3/PPh_3$ as catalyst. Under optimal conditions 1-dodecene gave 70% unbranched aldehyde, and 2-dodecene gave 55-60% [14].

The nature of the central metal of the catalyst plays the key role in determining the unusually high regioselectivities observed in the hydroformylation of 3,3,3-trifluoro propene (TFP) and pentafluorostyrene (PFS). With $Co_2(CO)_8$ as catalyst mainly normal aldehydes were obtained from TFP (93%) and PFS (79%) whereas $Rh_6(CO)_{16}$ furnished predominantly iso aldehydes (96% and 97%, respectively) [15].

Hydroformylation of $C_{10-13}$ alkenes, prepared by dehydrogenation of n-alkanes was examined. The amounts of straight chain aldehydes and alcohols formed were 3 times higher than the initial amount of 1-alkenes due to isomerization and higher reaction rate of 1-alkenes. Highest selectivity was obtained using a $Co_2(CO)_8$ + + $PBu_3$ catalyst [16]. The hydroformylation kinetics of $C_{11-14}$-olefins (formed by alkane dehydrogenation) by $HCo(CO)_3L$ complexes [L = $PBu_3$, $P(n\text{-}C_8H_{17})_3$ or $P(C_{12}H_{25})_3\text{-}P(C_{15}H_{31})_3$] was determined [17]. Modifying Co catalysts with ditertiary phosphines like diphos the concomitant isomerization is suppressed and therefore almost exclusively only those aldehydes are formed which correspond to the original position of the double bond in the employed olefin. The rate of reaction is strongly decreased, however [18]. The bridged cobalt carbonyl dimer $Co_2(CO)_6(dpm)$ has been used as a catalyst for the hydroformylation of 1-hexene at 120°C [19].

1- and 2-pentene hydroformylation was studied using $Co_4(CO)_{10}(PPh)_2$ and $Co_4(CO)_8(PPh_3)_2(PPh)_2$ catalysts. $Co_4(CO)_{10}(PPh)_2$ was re-isolated after 1000 turnovers in 95% yield [20]. The phosphido bridged cluster $Co_4(CO)_{10}(PPh)_2$ has been used as catalyst not only for hydroformylation, but also for CO hydrogenation and MeOH homologation. In all cases, however, this complex was less reactive than $Co_2(CO)_8$ [21].

As increasing amounts of $Fe(CO)_5$ were added, the catalytic activity of $HCo(CO)_3(PBu_3)$ in the hydroformylation of propylene passed through a minimum at the Fe/Co ratio of about 1. The formation of an inactive carbonyl-bridged complex containing Co, Fe and P was proposed [22].

b) Rh Catalysts

Ethylene and $H_2$ react with $Rh_4(CO)_{12}$ to form a complex [tentatively formulated as $HRh(CO)_3(C_2H_4)$] which is an active hydroformylation catalyst under mild conditions [23]. The use of $[Rh(COD)(L\text{-}L)](ClO_4)$ complexes (L-L = phenanthroline derivatives like 2,9-$Me_2$phen) as hydroformylation catalyst precursors was studied (50 bar, 80°C). No hydrogenation of olefins or aldehydes was observed but isomerization of the unreacted olefin was significant [24].

The kinetic equation

$$\frac{-d(\text{olefin})}{dt} = k[\text{olefin}][\text{Rh}]^{1/4}[P_{H_2}/P_{CO}]^{1/2}$$

has been obtained for the hydroformylation of 1-heptene in acetone with a $Rh_2(NBD)_2Cl_2$ + $PPh_3$ catalyst system (P:Rh = 11:1) at 40-100°C [25]. Allyl alcohol was continuously hydroformylated in the presence of $HRh(CO)(PPh_3)_3$ [26].

Catalysts formed by addition of $(p\text{-}RC_6H_4)_3P$ (R = Cl, F, H, Me, MeO) to $Rh_2(NBD)_2Cl_2$ are more selective in the hydroformylation of 1-heptene than $[(p\text{-}RC_6H_4)_3P]_2Rh(NBD)^+ClO_4^-$ complexes. This is due to increased catalytic isomerization of 1-heptene to cis- and trans--2-heptene with the perchlorate catalyst [27]. $Rh_2(Pz)_2[P(OPh)_3]_4$, $Rh_2(Pz)_2(CO)_2[P(OPh)_3]_2$ and $Rh_2(Me_xPz)_2(COD)_2$ complexes (Pz = pyrazolate) catalyze the hydroformylation of 1-heptene both in the presence and absence of $PPh_3$ at 80°C and 50 bar [28].

The hydroformylation of terminal olefins having an acetoxy, hydroxy or carboalkoxy substituent could be carried out even under 1 bar at 60-90°C when a small amount of $Ph_2P(CH_2)_4PPh_2$ (n = 2-4, diphosphine/Rh = 1/1-2/1) was added to the catalyst system composed of $HRh(CO)(PPh_3)_3$ and a large excess of $PPh_3$ [29]. The addition of such diphosphines to the conventional Rh catalyst system containing a large excess of $PPh_3$ was also beneficial in case of 1-octene hydroformylation. It decreased olefin isomerization, improved the thermal stability of the catalyst and reduced the inhibitory effects of $\alpha,\beta$-unsaturated aldehydes and $O_2$ [30].

Rhodium/phosphine catalyzed hydroformylation was studied using 1,1'-bis diphenylphosphino ferrocene and several derivatives containing substituents on the phenyl groups (p-Cl, m-F, p-$CF_3$). The most selective catalyst has three P atoms bound to each Rh atom. Electron withdrawing substituents afford higher rates and higher linear:branched aldehyde ratios [31].

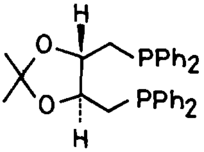
## c) Pt Catalysts

The deuteroformylation of Z- or E-2-butene, catalyzed by $Pt(DIOP)(SnCl_3)Cl$, gave predominantly erythro- or threo-1,3-$d_2$-2--methylbutanal, respectively. Thus, hydroformylation occured with cis-stereochemistry [32].

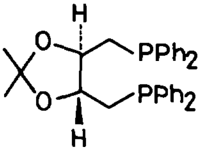
trans-$[Pt(COPr^n)(PPh_3)_2Cl]$ (which has been prepared from propene, cis-$Pt(PPh_3)_2Cl_2$ and CO in EtOH) catalyzes the hydroformylation of propene in the presence of $SnCl_2$ in methyl isobutyl ketone solution. trans-$Pt(COPr^n)(PPh_3)_2(SnCl_3)$ could be isolated from this reaction mixture. The latter complex is an active hydroformylation catalyst in methyl isobutyl ketone but no aldehyde is formed if EtOH is used as solvent [33]. Analogously, the complex trans--$[Pt(COC_6H_{13}\text{-}n)(PPh_3)_2Cl]$ has been synthesized from cis-$Pt(PPh_3)_2Cl_2$, CO and 1-hexene. In combination with $SnCl_2 \cdot 2H_2O$ this complex is also a hydroformylation catalyst [34]. The $Pt(PPh_3)_2Cl_2/SnCl_2$ catalyst system is not capable of hydroformylating internal olefins to terminal aldehydes. Using the cationic $[Pt(CO)(PR_3)_2Cl](ClO_4)/SnCl_2$ catalyst, significant amounts of terminal aldehydes are formed.

$ZnBr_2$ is also an effective modifier for this reaction [34a].

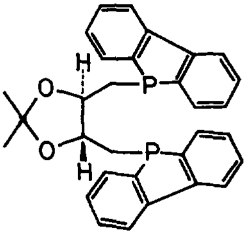
The $PtCl_2$-$SnCl_2$ complexes of (-)-DIOP (1b) and (-)-DIPHOL (2) were employed as catalysts in homogeneous asymmetric hydroformylations of styrene and high optical yields (ca. 94%) were obtained. Polymer-bound (-)-DIOP-$PtCl_2$-$SnCl_2$ gave optical yields of 25-30% [35].



1a, (+)-DIOP



1b, (-)-DIOP



2, (-)-DIPHOL

d) Other Metals

The hydroformylation of 1-hexene, 1-octene and $Me_3SiCH=CH_2$ is catalyzed by $M(CO)_5(SnCl_2)$, $M(CO)_5(SnO)$ or $M(CO)_6 + SnCl_2$ (M = Cr, Mo, W). Reaction conditions are 150-180°C and 200 bar ($H_2$:CO = 2:1), the activity of the complexes increases in the order Mo < Cr < W. Highest conversion of olefins was 71% in 10 hours [36]. The stoichiometric hydrogenation and hydroformylation of cyclopropenes with $HCo(CO)_4$ and $HMn(CO)_5$ led to similar products. Reactions with Co were significantly faster. The stereochemistry of the reactions suggests radical pairs as intermediates [37]. The cluster anion $HRu_3(CO)_{11}^-$ is a catalyst for the hydroformylation and hydrogenation of ethylene and propylene. Hydrogenation takes place at 25°C and 20 bar $H_2$ and is inhibited by CO. At 100°C and 40 bar ($1H_2$ + 2CO) hydroformylation is observed. Under $H_2$, the $HRu_3(CO)_{11}^-$ anion is transformed into a mixture of yet unidentified Ru carbonyl species, CO reconverts these into $HRu_3(CO)_{11}^-$ [38].

e) Heterogeneous Systems (Supported Complexes)

$Co_2(CO)_8$ was attached to a phosphinated silica surface and the interactions of CO, $H_2$ and propylene molecules with the attached cobalt carbonyl species studied by Raman spectroscopy. The observed spectra could be explained by the conventional mechanism of the hydroformylation reaction [39]. Anchored Co-carbonyl-phosphine complexes were prepared using silica treated with $(EtO)_2Si(CH_2CH_2CH_2PCy_2)_2$. Propylene hydroformylation experiments indicate that at low pressure (≈1 bar) Co complexes are not removed from the support and hydroformylation takes place on the anchored complexes [40]. The supported cobalt carbonyl cluster catalyst $SIL\text{-}SiCH_2CH_2CCo_3(CO)_9$ was prepared by bonding $Cl_3CCH_2CH_2Si(OEt)_3$ to a silica surface, followed by treatment with $Co_2(CO)_8$. This catalyst was used for hydroformylation of 1-heptene at 140°C and 40 bar. A high loss of Co was observed [41]. Pd and Co complexes were anchored on phosphinated silica prepared by treating silica with $(EtO)Si(CH_2CH_2CH_2PCy_2)_3$ and used as catalysts for the gas-phase hydroformylation of propene at 40-100°C and 1 bar CO. A strong synergetic effect was observed when Pd was introduced into the carbonylcobalt catalyst obtained from the phosphinated silica and $Co_2(CO)_8$ [42].

Poly(2,6-dimethyl-1,4-phenylene oxide) containing cyclopentadienyl ligands attached to the benzyl carbons was prepared and converted to polymer-bound $CpCo(CO)_2$, $CpRh(CO)_2$ and titanocene catalysts. The Co and Rh complexes were hydroformylation catalysts while the immobilized titanocene hydrogenated cyclohexene 10-70 times faster than the homogeneous analog [43].

The polymer-immobilized Rh complexes prepared from $RhCl_3$ or $Rh(CO)_2(acac)$ and chelate resins with iminodiacetic moieties had a catalytic activity for hydroformylation of 1-hexene in EtOH at 100°C under 20 bar of $H_2$ and 20 bar of CO. The normal/branched ratio in the aldehyde was 2.3 and 0.7, respectively [44]. Supported Rh(I) catalysts have been prepared by reacting polypropylene grafted p-styryldiphenylphosphine with $Rh(CO)_2(acac)$. In the hydroformylation of hexene-1 this catalyst with a P:Rh ratio of 8 gives a normal aldehyde:branched aldehyde ratio of about 16 at 65°C. This is much higher than that achieved with the corresponding homogeneous catalyst with $p\text{-}CH_2{=}CHC_6H_4PPh_2$ at the same P:Rh ratio [45]. Hexene-1 was hydroformylated with $Rh(CO)(PPh_3)_2Cl$ and its analogues anchored to alumina and silica. The supported complexes exhibited activity and selectivity similar to the homogeneous catalyst [46].

A $Rh(CO)(PPh_3)_2Cl$ type heterogenous catalyst was prepared by treating the $SiO_2$ carrier with $(EtO)_3SiCH_2CH_2PPh_2$ followed by complexing with $Rh_2(CO)_4Cl_2$. 1-Hexene was hydroformylated with this catalyst at 110°C and 40 bar to give 100% selectivity for heptanal with 95.7% conversion [47].

### f) Modified Hydroformylations

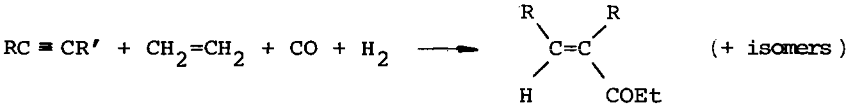
Hydroformylation of propene with CO, $H_2$ and a mixture of $Co_2(CO)_6(PBu_3)L$ and $Co_2(CO)_5(PBu_3)_2L$ (L = 2-aminopyridine) at 170°C and 40 bar followed by aldol condensation gave 80% yield of 2-ethylhexanol [48]. KOAc, $K_2CO_3$ and KOOCH were effective condensation agents for the preparation of 2-ethylhexanol from porpylene, $H_2$ and CO in the presence of $Co_2(CO)_8$ and $Bu_3P$ [49].

The hydroformylation of olefins by paraformaldehyde

$$RCH{=}CH_2 + \frac{1}{n}(CH_2O)_n \longrightarrow RCH_2CH_2CHO + \underset{\displaystyle CHO}{RCHCH_3}$$

is catalyzed by $H_2Rh(PPr^i_3)_2(O_2COH)$ at 120°C. At higher temperatures, alcohols and carboxylic acid methyl esters are formed as byproducts. The reaction is rather slow as compared to conventional hydroformylation with CO + $H_2$ [50].

Substituted acetylenes react with ethylene, CO and $H_2$ in the presence of $Rh_4(CO)_{12}$ catalyst:



R, R′ = H, Me, Bu, Ph, $CH_2OMe$, COOMe

Reaction conditions are 150°C and 60 bar ($C_2H_4/CO/H_2$ = 25/30/5), the regio- and stereospecificity of the reaction depends on R and R′ [51]. The synthesis of ketones from olefins and CO in the presence of alcohols as H-donors is catalyzed by $RuCl_3$ or base--promoted $Ru_3(CO)_{12}$ at 160-200°C and 10 bar. Alkoxycarbonylation and hydrogenation of the olefin are the main side reactions:

$$CH_2{=}CH_2 + CO + Me_2CHOH \longrightarrow EtCOEt,\ EtCOOPr^i,\ C_2H_6$$

The reaction rate is rather low [52].

## 3. Homologation of Alcohols and Esters with CO + $H_2$

A new catalyst system, consisting of $Fe(CO)_5$ and a tertiary amine has been developed for the homologation of MeOH to EtOH. Working conditions are 300 bar synthesis gas ($H_2$:CO : 1:2) and 200°C, EtOH is formed according the stoichiometry

$$CH_3OH + 2CO + H_2 \longrightarrow CH_3CH_2OH + CO_2$$

The following mechanism has been proposed:

$$\begin{aligned}
CH_3OH + CO &\xrightleftharpoons{R_3N(base)} HCOOCH_3\\
HCOOCH_3 + R_3N &\rightleftharpoons MeR_3N^+ + HCOO^-\\
Fe(CO)_5 + H_2 + R_3N &\rightleftharpoons HFe(CO)_4^- + CO + R_3NH^+\\
MeR_3N^+ + HFe(CO)_4^- &\longrightarrow H(Me)Fe(CO)_4 + R_3N\\
H(Me)Fe(CO)_4 + CO &\longrightarrow H(MeCO)Fe(CO)_4\\
H(MeCO)Fe(CO)_4 + CO &\longrightarrow MeCHO + Fe(CO)_5\\
MeCHO + H_2 &\xrightarrow{HFe(CO)_4^-} MeCH_2OH
\end{aligned}$$

$RhI_3$, $Ru_3(CO)_{12}$ and $Mn_2(CO)_{10}$ are also active catalysts under these conditions and the best results were achieved with a $Mn_2(CO)_{10}$ + + $Fe(CO)_5$ mixed system [53].

Complexes of Mn, Rh and Ru catalyze the homologation of methanol by CO + $H_2$ in the presence of tertiary amines at 300 bar and 200°C:

$$CH_3OH + H_2 + 2CO \longrightarrow CH_3CH_2OH + CO_2$$

The mixed $Fe(CO)_5$ + $Mn_2(CO)_{10}$ catalyst has been found to give the highest rate and the best selectivity for ethanol (the balance is methane)[54].

Acetaldehyde is the main product of methanol homologation with CO + $H_2$ if a $Co(OAc)_2.4H_2O$ + $PPh_3$ catalyst is used with HI as promoter at 180-200°C. A maximum for conversion and acetaldehyde selectivity is found at I:Co = 2:1, the effect of the P:Co ratio is much less pronounced [55]. The cobalt-catalyzed and iodide-promoted hydrocarbonylation of methanol to acetaldehyde

$$CH_3OH + CO + H_2 \longrightarrow CH_3CHO + H_2O$$

is significantly influenced by the nature of the iodide promoter the covalent MeI being much more active than ionic iodides like KI. Using both promoters a significant synergism could be observed [56].

Homologation of MeOH with $Co_2(CO)_8$ + $RuCl_3.nH_2O$ catalysts was studied. Both the yield and selectivity of EtOH were significantly dependent on the Ru/Co ratio and the composition of synthesis gas. Ethers such as 1-4-dioxane, THF, Me-cellosolve and diglyme served as good solvents to give higher yield (≈ 60%) and selectivity (≈ 80%) of EtOH [57].

The nature of the iodide promoter effects the selectivity of the Ru-catalyzed reactions of methyl acetate with CO and $H_2$. MeI favors the homologation reaction leading to ethyl acetate whereas alkali and ammonium iodides favor the simple carbonylation reaction to acetic acid [58]:

$$CH_3COOCH_3 + CO + 2\ H_2 \longrightarrow CH_3COOC_2H_5 + H_2O$$

$$CH_3COOCH_3 + CO + H_2O \longrightarrow 2\ CH_3COOH$$

In the homologation of methyl acetate the mixed clusters $(Et_4N)[RuCo_3(CO)_{12}]$ and $(Et_4N)[Ru_3Co(CO)_{13}]$ or a combination of $Ru(acac)_3$ and $Co_2(CO)_8$ were found to be more active catalysts for the formation of ethyl acetate than Ru or Co alone. Methyl iodide was used as a promoter [59].

## 4. Coordination Chemistry Related to CO Hydrogenation and Hydroformylation

Reduction of $[(\eta^5-C_5R_5)Re(NO)(CO)_2](BF_4)$ (R = H, Me) by $NaBH_4$ in $THF/H_2O$ afforded formyl, hydroxymethyl and methyl $(\eta^5-C_5R_5)Re(NO)(CO)R'$ (R' = CHO, $CH_2OH$, $CH_3$) derivatives. These two series of complexes are the first instances in which models for all presumed intermediates in CO reduction have been prepared [60]. Sodium cyanoborohydride ($NaBH_3CN$) in alcohols reduces a CO ligand on $CpFe(CO)_3^+$ via a hydroxymethyl intermediate to an alkoxymethyl ligand [61]:

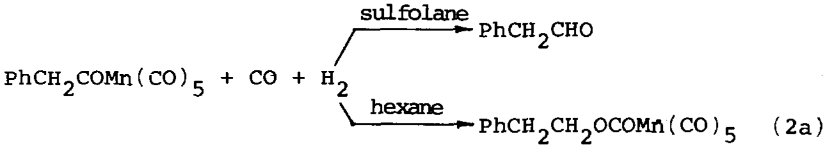
$$CpFe(CO)_3^+ \xrightarrow[ROH]{NaBH_3CN} CpFe(CO)_2CH_2OH \xrightarrow{ROH} CpFe(CO)_2CH_2OR$$

R = Me, Et 30-40%

The reactions of mono-, di-, tri-, tetra- and hexanuclear metal carbonyls with $HSO_3CF_3$ have been studied. Only tetra- and hexanuclear clusters produce significant amounts of $CH_4$ [61a].

A high-pressure IR-study has been made of the stability of some high-nuclearity carbonyl clusters of Ru and Os to CO and $H_2$. Reactions with CO tend towards the trinuclear species $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, while in reactions with $H_2$ the tetranuclear species $Ru_4H_4(CO)_{12}$ and $Os_4H_4(CO)_{12}$ seem to be the favored products [61b]. $^{13}C$-NMR measurements on Rh carbonyl clusters in solutions have been performed under high pressures of CO + $H_2$ (up to 1000 bar). It is shown, that $Rh_{12}(CO)_{30}^{2-}$ fragments into $Rh_5(CO)_{15}^-$ already at 5 bar of CO, but further fragmentation does not occur [62].

Reacting an acylmanganese pentacarbonyl with $H_2$ and CO different products are formed depending on the solvent (at 70°C and 80 bar):



$$PhCH_2COMn(CO)_5 + CO + H_2 \begin{cases} \xrightarrow{\text{sulfolane}} PhCH_2CHO \\ \xrightarrow{\text{hexane}} PhCH_2CH_2OCOMn(CO)_5 \end{cases} \quad (2a)$$

Treatment of (2a) with CO and $H_2$ at 200°C and 80 bar in the presence of $HMn(CO)_5$ yields the formate $PhCH_2CH_2OCHO$ [63]. Four distinct mechanisms have been established by kinetic measurements for the reactions between $p\text{-}MeOC_6H_4CH_2Mn(CO)_4L$ and $HMn(CO)_4L$ [L = CO or $(p\text{-}MeOC_6H_4)_3P$] leading to $p\text{-}MeOC_6H_4CH_3$ and/or $p\text{-}MeOC_6H_4CH_2CHO$. Some of the factors which influence the choice among these mechanisms (e.g. effect of L, solvent, or CO) have been identified [64].

The anion $EtFe(CO)_4^-$ reacts with $HFe(CO)_4^-$ to yield propionaldehyde in a smooth reaction:

$$EtFe(CO)_4^- + HFe(CO)_4^- \xrightarrow{0^\circ C} EtCHO \qquad 70\%$$

On the other hand the ethylation of the $HFe(CO)_4^-$ anion yields only ethane even under a high CO pressure:

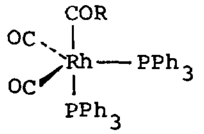
$$HFe(CO)_4^- + EtI \xrightarrow[25^\circ C]{100\ \text{bar CO}} EtH + Fe(CO)_5$$

These results suggest, that a binuclear mechanism may account for the formation of aldehydes in the Reppe hydroformylation process [65].

$HCo(CO)_4$ and styrene react in the presence of CO to form PhEt and $PhCHMeCOCo(CO)_4$, the kinetic data suggest a common radical pair intermediate for both reactions. The branched-chain acyl complex slowly isomerizes to the straight-chain isomer $PhCH_2COCo(CO)_4$ [66]. The exchange

$$HRh(CO)(PPh_3)_3 + n\ PPh_3 \rightleftharpoons HRh(CO)(PPh_3)_2 + (n+1)PPh_3$$

was studied at 5-105°C (n = 0-140) . In general the equilibrium favored the triphosphine rather than the biphosphine complex. The complexes of $Ph_2PCH_2CH_2PPh_2$ and $Ph_2P(CH_2)_3PPh_2$ prepared from the triphosphine rhodium complex by ligand exchange exhibited sharply reduced ligand exchange under comparitive conditions [67]. NMR--spectroscopic investigations indicate that the intermediate of hydroformylation with $HRh(CO)(PPh_3)_3$ as catalyst under ambient conditions is the square-planar cis-$HRh(CO)_2(PPh_3)$ [68]. This complex is trapped in the presence of olefins to form an acyl complex (3). In the case of octene-1 only one compound has been observed



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($R = n\text{-}C_8H_{17}$) but with styrene both possible isomers ($R = CH_2CH_2Ph$ and CHMePh) are formed, the branched-chain isomer being the primary product at 5°C which slowly isomerizes to the straight-chain isomer at 25°C [69]. In toluene solutions of $Rh(CO)_2(acac)$ or $HRh(CO)(PPh_3)_3$ containing $PPh_3$ the complexes $HRh(CO)_2(PPh_3)_2$ and $Rh_2(CO)_2(PPh_3)_4$ were identified in presence of $H_2$ and CO at -35 to -90°C by $^{31}P$-NMR. Based on these results also complex (3) was proposed as the intermediate of hydroformylation [70].

## 5. Water Gas Shift Reaction

Based on preparative experiments leading to $M(CO)_5(OOCH)^-$ type formato complexes (M = Cr, Mo, W) it has been proposed, that the premier mechanistic step in the thermal catalysis of the water gas shift reaction by group 6B metal carbonyls entails the nucleophilic attack of a CO ligand by the hydroxide ion leading to a metallocarboxylic acid $M(CO)_5(COOH)^-$ [71]. Under photocatalytic conditions, however, the loss of a CO ligand is the first step followed by the reaction with formate (formed from CO and $OH^-$) in solution to yield a formate complex [72]:

$$M(CO)_6 \xrightarrow{-CO} M(CO)_5 \xrightarrow{HCOO^-} M(CO)_5(OOCH)^-$$

It was shown, that the anion $Mo(CO)_5(OOCH)^-$ is present during the water gas shift reaction in basic media and has been proposed as a likely catalytic intermediate [73].

The kinetics of the following two reactions and have been determined:

$$Fe(CO)_5 + OH^- \longrightarrow HFe(CO)_4^- + CO_2$$

$$4\ H_2Fe(CO)_4 \longrightarrow 3\ H_2 + H_2Fe_3(CO)_{11} + Fe(CO)_5$$

In the water-gas shift reaction, $Fe(CO)_5$ is a poor catalyst because of the conflicting pH requirements of these two steps involved in the catalytic cycle [74]. The kinetics of methoxy- and hydroxycarbonyl adduct formation from $Ru(CO)_5$, $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$ have been determined (R = H,Me):

$$M_x(CO)_y + OR^- \longrightarrow M_x(CO)_{y-1}(COOR)^-$$

The three substrates are $10^3$-$10^4$ times more reactive against these oxygen nucleophiles in comparison to $Fe(CO)_5$. This explains the much higher catalytic activity of $Ru(CO)_5$ in the water gas shift reaction as compared to $Fe(CO)_5$ [75].

The trinuclear Ru clusters $Ru_3(CO)_{12}$ and $HRu_3(CO)_{11}^-$ were shown to play the major role in catalysis of the water gas shift reaction in basic media irrespective of whether the reaction is initiated by tetranuclear or trinuclear Ru carbonylates. $H_2$ inhibits this catalytic system in accordance with the equilibrium [76]:

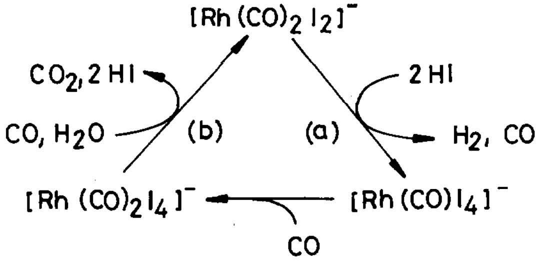
$$3\ H_3Ru_4(CO)_{12}^- + 9\ CO \rightleftharpoons 3\ HRu_3(CO)_{11}^- + Ru_3(CO)_{12} + 3\ H_2$$

The complexes [Ru(CO)(N-N)Cl]Cl [(N-N = bpy or phen] were shown to be active catalytic species for the water gas shift reaction under illumination with white light (100-160°C, 1-3 bar CO). The rate determining step is the photochemical loss of $H_2$ from $H_2Ru(bpy)_2Cl^+$, while $CO_2$ is produced thermally [77]. Os and Ru cluster carbonyls were anchored on cross-linked polystyrene through metal-C bonds and their catalytic activities for the water gas shift reaction studied [78].

Several side reactions occur under the conditions of the carbonylation of methanol to acetic acid in the presence of Rh or Ir catalysts. Of these the water gas shift reaction (with Rh) and the formation of methane (with Ir):

$$CH_3OH + CO \longrightarrow CH_4 + CO_2$$

has been studied. The following mechanism has been proposed for the water gas shift reaction:



At low acidity step (a) whereas at high acidity step (b) becomes rate controling. This is in agreement with the observation that the rate shows a maximum with the Hammett acidity function ($H_o$) [79].

The A-frame complex $(\mu\text{-H})Rh_2(\mu\text{-CO})(CO)_2(dpm)_2^+$ catalyzes the water has shift reaction, the hydroformylation of ethylene to propanal by CO + $H_2O$, and the hydrogenation of ethylene to ethane and propanal to propanol by $H_2$ at 90°C and 1 bar. The nearly identical rates of the water gas shift reaction and hydroformylation suggest similar slow steps [80].

$[H_3Pt_2(Ph_2PCH_2PPh_2)_2](PF_6)$ catalyzes the water gas shift reaction at 100°C, the turnover rate is considerably higher at lower pressures of CO. Tetranuclear clusters are formed during the reaction in the catalytic solutions [81].

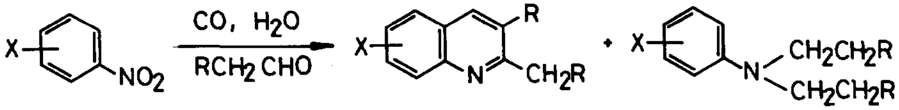
## 6. Reductions with CO + $H_2O$

The $H_2Rh(PPr^i_3)_2(O_2COH)$ complex was attached to a phosphinated silica prepared from $Ph_2P(CH_2)_3Si(OMe)_3$ and used for the hydrogenation of Me cinnamate with CO and $H_2O$. The heterogenized catalyst can be repeatedly reused with some loss of activity [82].

The $Rh_6(CO)_{16}$ + $Me_2N(CH_2)_3NMe_2$ catalyst system has high activity for the reduction of aldehydes using CO and $H_2O$ as the H source at

80°C and 5 bar. Unsaturated aldehydes give the corresponding unsaturated alcohols in high yield (80-100%)[85].

Nitrogen heterocycles like quinoline or phen are partially hydrogenated by CO + $H_2O$ in presence of $Fe(CO)_5$ and KOH at 42 bar and 150°C. The catalyst system is also active for the hydrogenation of anthracene to the 9,10 dihydro derivative. This hydrogenation is enhanced by phase transfer agents [84]. A wide variety of Mn, Fe, Ru and Co carbonyl compounds were tried as catalysts for the reduction of polynuclear heteroaromatic N compounds using water gas shift (CO, $H_2O$, base) and synthesis gas ($CO{:}H_2$ = 1:1) conditions. In most cases only the N containing ring was hydrogenated [85]. Nitroarenes are reductively N-alkylated and transformed into N-heterocycles with aldehydes, CO and $H_2O$ in the presence of Rh and Pd complexes at 180°C and 70 bar:



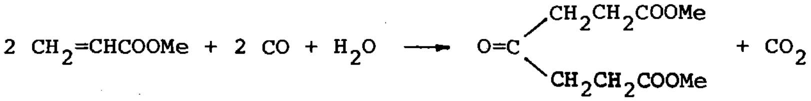
R = Me, Et, Pr
X = H, Me, Cl, MeO

Best results were achieved with the binary catalyst $Rh(PPh_3)_3Cl$ + $PdCl_2$ [86]. Oxidized N compounds are reduced by CO + $H_2O$ with $[Ru(COD)(py)_4](BPh_4)_2$ as catalyst at 100-140°C and 10-80 bar. Aromatic and tertiary aliphatic nitro compounds yield amines, secondary and primary aliphatic nitro compounds ketones (via oximes) and amides, respectively [87].

## 7. Reactions of Olefins with CO + $H_2O$

Styrene is hydrogenated and hydroformylated by CO and $H_2O$ in the presence of a $Fe_3(CO)_{12}$ + $Et_3N$ + NaOH catalyst system at 140°C and 100 bar in $H_2O$/MeOH. 1,3-Diphenylbutane is formed as a by-product [88].

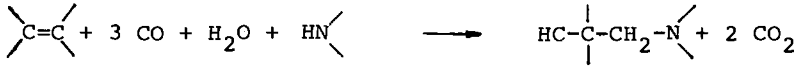
Methyl acrylate is hydrocarbonylated to dimethyl 4-oxopimelate by CO + $H_2O$ with the $Co_2(CO)_8$ + diphos catalyst system at 135°C and 70 bar [89]:



$$2\ CH_2{=}CHCOOMe + 2\ CO + H_2O \longrightarrow O{=}C\begin{matrix} \diagup CH_2CH_2COOMe \\ \diagdown CH_2CH_2COOMe \end{matrix} + CO_2$$

Rhodium complexes like $Rh_6(CO)_{16}$ catalyze the synthesis of tertiary and secondary amines from olefins, CO, $H_2O$ and amines or

$NH_3$ at 140°C and 70 bar [90]:



Aldehyde formed from the olefin by hydroformylation is supposed as an intermediate. Enamines and Schiff bases are hydrogenated to saturated amines under the same conditions [90].

## III. Hydrogenation and Reduction

### 1. H-D Exchange

Irradiation of a solution of $(C_5Me_5)Ir(CO)_2$ in neopentane at room temperature resulted in the formation of $(C_5Me_5)Ir(CO)(H)(CH_2CMe_3)$. The oxidative addition of such an unactivated $sp^3$ C-H bond has not been observed yet although it has been proposed as a step in the catalysis of H-D exchange by transition metal complexes [91].

The rate constants of oxidation and H-D exchange of cyclohexane in aqueous Pt(II) - Pt(IV) chloride solutions were determined [92]. H-D exchange between benzene and $C_2D_4$ in the presence of vanadocene at 70°C gave mainly $C_6D_6$; similar exchange with $CH_4$ gave mostly $CH_3D$. Results indicate that the reactions involve oxidative addition of the hydrocarbons to vanadocene [93]. Ortho-deuterated aromatic carboxylic acids and β-deuterated α, β-unsaturated carboxylic acids may be prepared with high regioselectivity by exchange deuteration of the unlabelled acids with $D_2O$ in the presence of $RhCl_3.3H_2O$ at 110°C [94].

### 2. Hydrogenation of Olefins

#### a Fe, Ru and Os Catalysts

Laser photocatalytic hydrogenation of 1-pentene with $Fe(CO)_5$ was studied. The quantum yield was about twenty. $Fe(CO)_3$ is regarded as the catalyst [95]. The hydrogenation of allylbenzene was studied using iron complexes supported on a polymer containing phosphonite or phosphonate groups. The catalysts with phosphonite groups are more selective but less active than the catalysts with phosphonate groups [96].

The cluster $H_4Ru_4(CO)_{12}$ acts as a catalyst for ethylene hydrogenation in heptane solution at 72°C. Detailed kinetic measurements and spectral investigations support metal cluster catalysis with $H_3Ru_4(CO)_{11}(C_2H_5)$ as an intermediate:

$$H_4Ru_4(CO)_{12} \rightleftharpoons H_4Ru_4(CO)_{11} + CO$$
$$H_4Ru_4(CO)_{11} + H_2 \rightleftharpoons H_6Ru_4(CO)_{11}$$
$$H_4Ru_4(CO)_{11} + C_2H_4 \rightleftharpoons H_3Ru_4(CO)_{11}(C_2H_5)$$
$$H_3Ru_4(CO)_{11}(C_2H_5)+H_2 \longrightarrow H_4Ru_4(CO)_{11} + C_2H_6$$

In the presence of $D_2$ a rapid H-D exchange between reactants takes place to give $C_2H_3D$ and HD [97]. The photocatalyzed hydrogenation of ethylene by $H_4Ru_4(CO)_{12}$ was reported. The quantum yield for ethane formation was 1.8 and the reaction was inhibited by CO. The $Ru_4$ cluster framework seems to provide the catalytic sites [98].

The hydrogenation of olefins is catalyzed by $RuPt_2$, $Ru_2Pt$, $Fe_2Pt$ and $Os_3$ clusters on $Ph_2P$ group containing polymeric or silica supports [99]. The reaction between $Os_3(CO)_{12}$ and silica gives the grafted cluster $HOs_3(CO)_{10}(OSi\leftarrow)$ which is a catalyst for ethylene hydrogenation at 80°C. Several intermediates of the catalytic cycle have been observed by infrared spectroscopy [100].

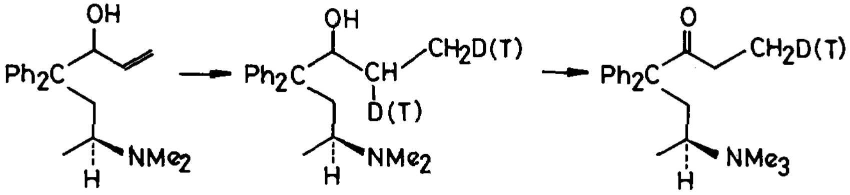
b) Co, Rh and Ir Catalysts

The coupled hydrogenation of PhR (R = H, Me, Et) and olefins (styrene, cyclohexene, cyclohexadiene, 1-hexene, 1,3-butadiene, isoprene) was studied with catalysts consisting of Co complexes, $Bu_3P$, and Al compounds or Grignard reagents. PhR was hydrogenated to cyclohexanes and cyclohexenes; the selectivity for cyclohexene from benzene reached 70%. NMR data indicated that $H_3Co(PBu_3)_3$ was formed in a $Co(acac)_2$ + $HAl(CH_2CHMe_2)_2$ + $Bu_3P$ system [101]. The reaction of $NaBH_4$ with complexes of N,N-diethylnicotinamide with $CoCl_2$, $NiCl_2$ and $RhCl_3$ gave catalysts for the hydrogenation of 2-methyl-1,3-butadiene, allylbenzene, and Me linoleate. The activity of the catalysts increased in the order Co < Ni < Rh [102].

Co-condensation of Rh vapours and toluene at liquid $N_2$ temperature followed by warming to about -50°C gives a red-brown solution which is a good catalyst for the hydrogenation of olefins at room temperature. When all olefin has reacted a brown precipitate is formed (a metal cluster species containing organics) which catalyzes the hydrogenation of aromatic hydrocarbons [103]. $[(C_5Me_5Rh)_2(OH)_3]Cl$ (A) is an effective olefin hydrogenation catalyst. It can be activated to become even more efficient either by exposure of its solution to air (which burns off some $C_5Me_5$ ligand) or by addition of small amounts of Rh complexes which do not contain stronly bound ligands. The best homogeneous catalyst contains 80% (A) and 20% $Rh_2(COD)_2Cl_2$

(B). Catalysts with a higher proportion of (B) were heterogeneous [104].

Examination of Rh(PPh$_3$)$_3$Cl as a catalyst precursor by ESCA revealed Rh(I) and Rh(III) species in the catalyst. The ratio of Rh(I) to Rh(III) was 3:2 regardless of the source of the compound (commercial or laboratory preparations). Hydrogenation of cyclohexene was performed to determine the effect of the higher binding energy species on the catalytic activity [105]. The hydrogenation of cyclohexene and hexene-1 with Rh(PPh$_3$)$_3$Cl as catalyst is accelerated by a factor of 1.7 by photolysis [106]. Selective 1,2-deuteration and tritiation of 1,2-dehydro methadol (4) and some derivatives was performed with Rh(PPh$_3$)$_3$Cl as catalyst. Oxidation of the labeled methadols (5) with pyridinium chlorochromate followed by treatment with aqueous NaOH to remove labile $\alpha$-D(T) furnished 1-D(T) methadone (6) [107]:



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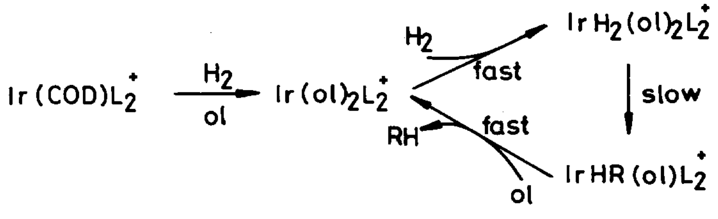
[Rh(NO)(PPh$_3$)$_2$L] (L = p-benzoquinone) catalyzes the hydrogenation of 1-hexene, cyclohexene, and styrene, as well as the selective hydrogenation of 1,3-cyclohexadiene to cyclohexene. The catalytic activity of the complex is low [108]. The complexes cis- and trans-Rh(CO)L$_2$Cl (L = 2-morpholino-, piperidino-, diphenylamino-, diethylamino- and dimethylamino-1,3,2-dioxaphosphorinane) were prepared. Only the trans isomers are active in the hydrogenation (and isomerization) of 1-heptene at 70$^{\circ}$C under 1 bar H$_2$ pressure [109]. Aqueous or methanolic solutions of the complexes obtained from Rh$_2$(NBD)$_2$Cl$_2$, Ph$_2$PCH$_2$CH$_2$NMe$_3^+$NO$_3^-$ and H$_2$ catalyze the hydrogenation of water-soluble and water-immiscible olefins in one- or two-phase systems, respectively. Addition of a macroreticular cation exchange resin results in a supported catalyst which shows negligible leaching and from which the Rh can be quantitatively recovered with HClO$_4$ [110].

Rh(ttp)Cl in the presence of $Et_3Al$ is an effective homogeneous catalyst for hydrogenation of 1-olefins and 1-octyne. A mechanism involving RRh(ttp), HRh(ttp) associated with an ethylaluminium species and $H_2$ is proposed to account for the spectroscopic and kinetic data [110a]. The observed rate of hydrogenation of 1-octene to octane at 20°C is 25 times higher than with $Rh(PPh_3)_3Cl$ under comparable conditions [111].

The insoluble polymer $(Rh(CO)[(CN)_2C_6H_4]Cl)_4$ prepared from $Rh_2(CO)_4Cl_2$ and 1,4-diisocyanobenzene catalyzes the hydrogenation and isomerization of 1-hexene. These reactions are retarded by light but the initiation of hydrogenation is a photoassisted process [112]. Rh bound on phosphinated or sulphonated polystyrenes and polyimine-type chelate resin catalyzes olefin isomerization and hydrogenation. The oxidation state of the metal was determined by XPS and found to be close to Rh(I) [113].

The catalytic activity of complexes of Rh(III) with polyethyleneimine in cyclohexene hydrogenation increases after repeated use and depends on the amount of Rh(I) present [114]. Polymeric hydrogenation catalysts for alkene and benzene were prepared by treating PVC with $HCONMe_2$, supporting the product on $SiO_2$, and treating it with $RhCl_3.3H_2O$. The activity of the complex is higher than that of polyamide-metal complexes or other polymeric complexes for the hydrogenation of benzene and cycloolefins under mild conditions [115]. Rh(I) complexes fixed on silica gel were prepared by exposing first the ligand $(EtO)_3Si(CH_2)_nPPh_2$ (n = 1-6) and then the Rh(I) salt in solution to the silica gel support. The effect of support porosity and the degree of its surface saturation were studied on the activity and stability of the prepared catalysts in hydrogenation of alkenes [116].

Several tests establish the homogeneity of the $[Ir(COD)(PPh_3)_2](BF_4)$ alkene hydrogenation (and dehydrogenation) catalyst. Based primarily on NMR spectroscopic results the following mechanism has been proposed for olefin hydrogenation with this catalyst (L = $PPh_3$, ol = olefin) [117]:



$Ir(CO)(Ph_3P)_2Cl$ did not catalyze the hydrogenation of acrylonitrile at room temperature, but at 80°C under pressure the reaction was fairly rapid [118]. The hydrogenation of 1-hexene in solutions containing $[M(diolefin)(P(p\text{-}MeOC_6H_4)_3)_2](ClO_4)$ (M = Rh, Ir) is fastest in 2-methoxy ethanol and in benzene and slowest in dichloromethane. The complexes show high selectivities in the hydrogenation of 3-hexyne and several diolefins to monoolefins [119]. The carboranyliridium complex $[Ir(\sigma\text{-carb})(CO)(PhCN)(PPh_3)]$, where carb = $-7\text{-Ph-}1,2\text{-}C_2B_{10}H_{10}$, was found to be an effective catalyst for homogeneous hydrogenation of α-olefins and acetylenes. Double bond isomerization is negligible and internal olefins are not hydrogenated [120].

### c) Pd and Pt Catalysts

Several compounds of Pd(II), Pd(I) and Pd(O) with the ratio $P:Pd \geqslant 1$ were found to be inactive as hydrogenation catalysts if no $O_2$ was present. In presence of $O_2$, $H_2O_2$ is formed which oxidizes part of the $PPh_3$ and enables the formation of $Pd_5(PPh)_2$ which is an active catalyst for the hydrogenation of many organic compounds containing double bonds. The same catalytically active complex is formed also from $Pd_2(PPh_3)_2$ and $[Pd(OAc)_2]_3$ under $H_2$ in which case no $O_2$ is necessary to activate the system [121,122]:

$$Pd_2(PPh_3)_2 + [Pd(OAc)_2]_3 + 4.5\ H_2 \longrightarrow Pd_5(PPh)_2 + 3PhH + 6\ AcOH$$

The complex $[Pd_5(phen)_2(OAc)]_n$ catalyzes the hydrogenation of allyl alcohol and 1,3-pentadiene [123].

A poly-γ-(m-diphenylphosphinophenyl)propylsiloxane-Pd complex was prepared by treating the polymer with $Na_2PdCl_4.4H_2O$. The complex exhibits high activity and selectivity in hydrogenation of olefins. It can be reused without serious loss of activity [124]. The same Pd complex catalyst supported on colloidal $SiO_2$ is useful for the hydrogenation of ethylenic double bonds having aromatic, -CN, -COOR substituents. Cyclopentadiene, isoprene, or α-pinene are not hydrogenated [125]. An XPS study of a poly methylphenylsilazasiloxane-Pd complex showed 2 lone pairs of electrons on 2 N atoms and 1 Pd atom. Inactivation of the complex in the hydrogenation of olefins is caused by the reduction of Pd(II) to Pd(O) [126].

Poly [4-(2)-vinylpyridine]-$PdCl_2$ complexes are effective hydrogenation catalysts for olefins at 30°C and 1 bar $H_2$ pressure. The complexes are stable in air and can be easily recovered, and repeatedly used without loss of activity [127]. Pd chelates with 5-amino-2-(2-hydroxy-4- and -5-aminophenyl)benzoxazole-terephthaloyl chloride copolymer polyamide fibers catalyze the hydrogenation of 1-hexene, 1,3-pentadiene, allyl benzene, and Me linoleate. The dienes give a 1:1 mixture of the corresponding olefins and paraffin [128].

Palladium complexes containing 1-6 Pd atoms, fixed on silica gel catalyze the hydrogenation of 3-sulfolene to sulfolane and of thiophene to thiophane at 20°C and 1 bar [129]. Pd-phosphine cluster complexes were fixed on silica gel and their catalytic activity tested in the disproportionation of cyclohexene and the hydrogenation of cyclopentadiene and cyclopentene [130].

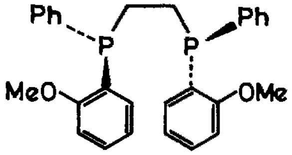
Silica-supported poly-$\gamma$-diphenylphosphinopropylsiloxane-Pt complex is a highly active and selective catalyst for the hydrogenation of alkenes at room temperature and atmospheric pressure, and can be reused 30 times without any appreciable loss in catalytic activity [131]. Treatment of $(Ph_3P)_2PtO_2$ with $H_2$ in $C_6H_6$ at 65°C gave a dark brown amorphous complex, $Ph_3PPtO$, which exhibited catalytic activity in the hydrogenation and isomerization of olefins. The addition of $PPh_3$ inhibited hydrogenation but increased selectivity for hydrogenation [132].

### d) Other Metals

Irradiation of $H_4M(diphos)_2$ (where M = Mo, W) in the presence of an alkene like 1- or 2-pentene results in stoichiometric reduction to form alkane. In an atmosphere of $H_2$ catalytic hydrogenation occurs, 1-pentene turnover numbers above 150 have been observed [133]. Metallophthalocyanines are active as catalysts in the hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline at 300-400°C and 70-200 bar $H_2$. Little or no hydrogenolysis of the product is observed [134]. The reaction of $Cu(st)_2$ with $Et_3Al$ formed a soluble catalyst which promoted the selective hydrogenation of linolenyl groups in soybean oil. The activity was enhanced by the addition of $SiO_2$, $Al_2O_3$ or $TiO_2$. More active and in some cases more selective catalysts were formed when $Et_3Al$ was replaced by $R_3Al$ compounds containing longer chain alkyl groups. Among other organometallics tested $Et_2Mg$ and $(iBu)_2AlOEt$ formed active catalysts [135].

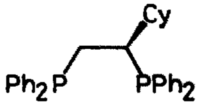
## 3. Asymmetric Hydrogenation of Olefins

The complexes formed from the asymmetric hydrogenation catalysts $Rh(P-P)(MeOH)_2^+$ [(P-P) = (-)-DIOP (1b) or diPAMP (7)] and $\alpha,\beta$-unsaturated acids were investigated by $^{31}P$ NMR spectroscopy. The DIOP-complex (a 7-membered chelate) forms preferentially complexes in which olefin and carboxylate are bound to the metal. In related experiments with diPAMP 2-methylenesuccinic acid gave a variety of complexes including tridentate species where both carboxyl groups and olefin were concomitantly bound [136].



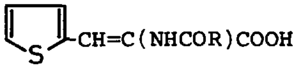
7, (R,R)-diPAMP

Enamiderhodium complexes formed by the six- and seven-ring chelate-forming biphosphines (-)-DIOP (1b), $Ph_2P(CH_2)_3PPh_2$ and $Ph_2P(CH_3)_4PPh_2$ have been investigated by $^{31}P$ and $^{13}C$-NMR spectroscopy. Derivatives of Z-dehydroamino-acids are co-ordinated to Rh through olefin and amide, whereas derivatives of E-dehydroamino--acids through olefin and carboxylate groups. Latter arrangement is inferior in effecting enantioselection leading to lower optical yields in hydrogenation [137]. When the asymmetric hydrogenation catalyst precursor $[Rh(NBD)(cycphos)](PF_6)$ is hydrogenated in $CH_2Cl_2$, a non-donor solvent, dimeric $[Rh(cycphos)]_2(PF_6)_2$ results [(R)-cycphos see (8)]. This complex is a $\pi$-arene bridged species and may be present in low levels also in a donor solvent, such as MeOH [138].



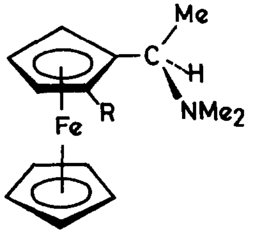
(R)-cycphos 8

Dehydroaminoacids containing a thiophene ring (9) were hydrogenated with Rh(I) complexes of (+)-and (-)-DIOP (1a and 1b) as catalysts. The Z-acids gave quantitative conversion and enantiomeric excess up to 78%. The catalyst was apparently insensitive to poisoning by the thiophene sulfur [139].



(R = Me,Ph) 9

[Rh(COD)$L_2$]($BF_4$) [L = optically active $Ph_2PCHMeR$ (R = Et, iPr)] complexes catalyzed the hydrogenation of E-PhCH=CMeCOOH, E-MeCH==CMe-COOH and CH=CEtPh to give the (R)-isomer with optical yields of 1-13% [140]. The cationic Rh(I) complexes of the chiral ligands (10a) and (10b) catalyze the asymmetric hydrogenation of acetamidoacrylic acid derivatives and itaconic acid. The configuration of the product is reversed if (10b) is used instead of (10a) and the reaction is faster and the optical yields higher (84%) with the former ligand. The ligands (10c) and (10d) give catalytically inactive Rh(I) complexes [141].



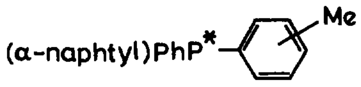
10a, R = $PBu^t_2$

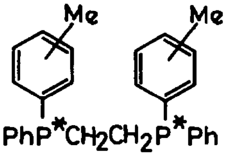
10b, R = $PPh_2$

10c, R = $AsPh_2$

10d, R = $AsMe_2$

The chiral ligands (11)-(13) were prepared and used as Rh(COD)$(L)_2^+$ [L = (11)] or Rh(COD)$(L_2)^+$ [$L_2$ = (12), (13)] complexes for the asymmetric hydrogenation of α-acetamidoacrylic acid. Highest optical yields (76%) were achieved with (13) [142].

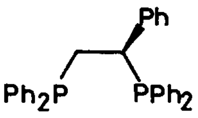




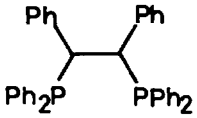
11, o- and p-isomers

12, o- and p-isomers

(R)-Phenphos (14) has been synthesized in good overall yield from (S)-mandelic acid. Optical yields up to 88% have been observed with this ligand in catalytic asymmetric hydrogenation. The Rh complexes of this chiral phosphine and those of racemic (15) and (16) with dehydroamino-acids have been investigated by $^{31}$P-NMR spectroscopy [143].



(R)- phenphos, 14



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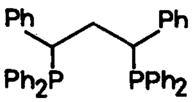
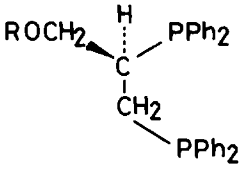


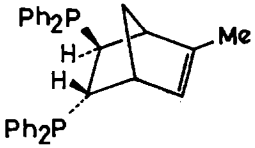
16

The chiral 1,2-diphosphine ligands (17)-(20) have been synthesized. Rh(NBD)(diphosphine)$^+$ complexes containing (17), (18) [144] or 20 [145] as ligands were found to be effective catalysts for the asymmetric hydrogenation of dehydro amino acids and similar prochiral olefins (optical yields up to 92%). The corresponding Rh complex of (19) was practically inactive as a hydrogenation catalyst [144] and low optical yields were observed for the hydrogenation of $CH_2=CRCOOH$ (R = $CH_2COOH$, Ph) with (17) and (20) [145].



17, R = $PhCH_2$
18, R = tBu
19, R = H
20, R = $CPh_3$

(+) and (-) MeNorphos (21) and (22) were prepared and used as optically active ligands in asymmetric hydrogenation with catalysts obtained in situ from $Rh_2(COD)_2Cl_2$ and the phosphine. (Z)-α-(N-acetamido)cinnamic acid and itaconic acid are hydrogenated with 92 and 60% enantiomeric excess, respectively [145a].



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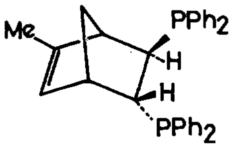
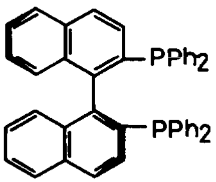


22

A number of chiral biphosphines related to (R,R)diPAMP (7) were prepared and evaluated in asymmetric hydrogenation with Rh complexes. Many variants were closely equivalent but none was superior to the parent compound. Some monophosphines containing sulfone substituents permitted to use them in aqueous solutions. Several new DIOP analogs were tried in the hydroformylation of $CH_2=CHOAc$ but only modest enantiomeric excesses were achieved [146].

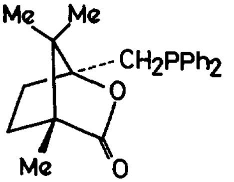
The axially dissymmetric bisphosphine (23) yields efficient catalysts for the asymmetric hydrogenation of α-aminoacrylic acids and esters, with optical yields up to 98% [147].



(S) - 23

The structure and absolute configuration of Rh(NBD)[(+)-589-(R)-2,2'-bis(diphenylphosphino -1,1'-binaphtyl]$(ClO_4)$, the precursor of an enantioselective hydrogenation catalyst was determined [148]. The ditertiary phosphine 2,2'-bis(diphenylphosphino)biphenyl was used as a ligand in hydrogenating dehydroamino acids with Rh complexes as catalysts. By the use of the (+) 589 form of this ligand modest optical yields ( < 13%) were achieved [149].

The chiral phosphine (24) and phosphinite (25) were prepared and used a ligands in Rh based complex catalysts for the asymmetric hydrogenation of prochiral unsaturated carboxylic acids. Optical yields did not exceed 35% [150].



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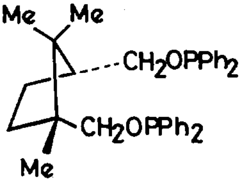
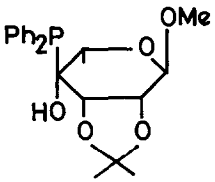


25

The chiral phosphorous ligands (26-30) were prepared starting from carbohydrates. Homogeneous asymmetric hydrogenations of several prochiral olefins were carried out using Rh(I) complexes of these ligands formed <u>in situ</u>. Optical yields of 29-67% were achieved with the ligand (30) [151].



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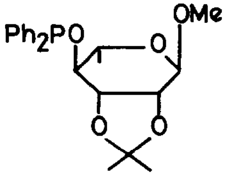

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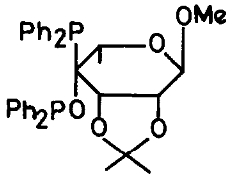

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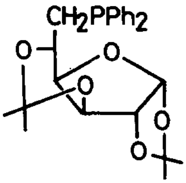

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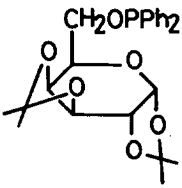
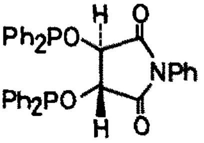


30

The two chiral diphosphinites (31) and (32) were prepared from tartaric acid and used as ligands for the preparation of the complexes $[RhL_2Cl]_2$ ($L_2$ = 31 or 32). These complexes were used as catalysts for the asymmetric hydrogenation of dehydroamino acids, citraconic acid and 2-phenyl-1-butene [152].



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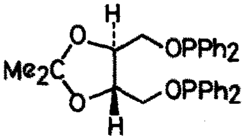
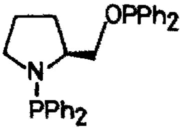


32

The chiral aminophosphine-phosphinites (S)-prolophos (33) and (S)-butaphos (34) have been prepared. The Rh(I) complexes of these ligands $Rh(COD)(L_2)^+$ ($L_2$ = 33 or 34) have been used as catalysts for the asymmetric hydrogenation of α-acetamido acrylic acid, α-acetamido cinnamic acid and itaconic acid [153].



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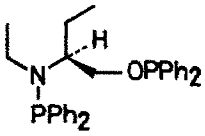
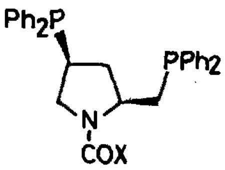


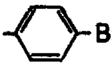
34

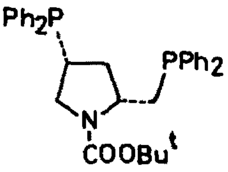
$Rh_2(COD)_2Cl_2$ and $Rh_2(CO)_4Cl_2$ react with 1,2:3,4-di-O-isopropylidene-β-D-galactopyranose 6-(Et phosphite) and 6-deoxy-1,2-O-isopropylidene-β-D-glucofuranose cyclic 3,5-phosphite to give Rh(I)complexes which are hydrogenation catalysts for itaconic and α-acetamido cinnamic acids [154].

Asymmetric hydrogenation of various dehydro dipeptides was carried out using Rh complex catalysts with a variety of chiral diphosphine ligands. Pyrrolidinodiphosphines [e.g. Ph-CAPP (35), p-BrPh-CAPP (36) (+)-and (-)-BPPM (37a and b) and diPAMP (7) exhibited excellent stereoselectivities, whereas (+)- and (-)-DIOP (1a and 1b), chiraphos (38), prophos (39) and BPPFA (40) gave only poor results. Accordingly, a series of new chiral pyrrolidinodiphosphines were prepared (41a-h) in which the N-atom of (+)-PPM (42) is linked up with a variety of α-aminoacyl groups. The stereoselectivities attained by these α-AacPPMs are as high as those obtained with other pyrrolidinodiphosphines [155].



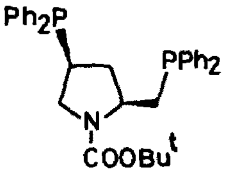
35, X = NHPh

36, X = NH--Br



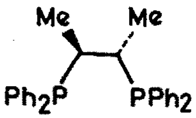
(+)- BPPM

37a



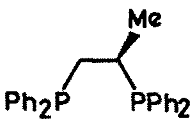
(-)- BPPM

37b



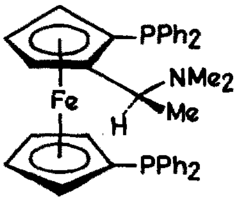
(S,S)-chiraphos

38



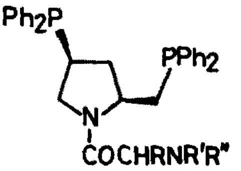
(R) - prophos

39



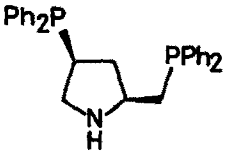
BPPFA

40



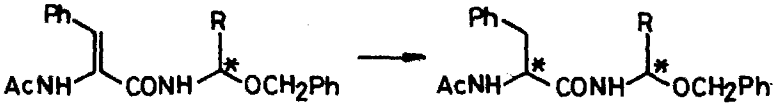
41

R = H, alkyl, $PhCH_2$
R' = H, Z-(S)-phenylalanyl
R" = Z,H



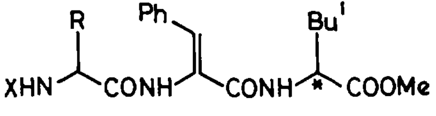
42, (+)-PPM

The chiral N-(N-acetyldehydrophenylalanyl)- β-amino alcohol benzyl ethers (43) were hydrogenated with Rh catalysts containing chiral or achiral phosphine ligands:



43, R = $PhCH_2$, iBu, iPr, $CH_2CH_2SMe$

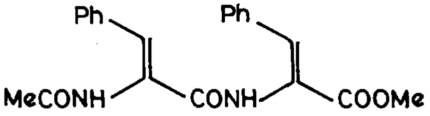
High double asymmetric inductions (77-97%) were achieved with Ph-CAPP (35), (+)-BPPM (37a), (+)-and (-)-DIOP (1a and 1b) as chiral ligands [156]. Dehydrotripeptides (44) were employed as substrates in the asymmetric hydrogenation catalyzed by cationic chiral Rh-diphosphine complexes $Rh(NBD)(L_2)^+$ ($L_2$ = (+)- and (-)--BPPM (37a and 37b), (+)- and (-)-DIOP (1a and 1b), Ph-CAPP (35) and diPAMP (7) . Enantioselectivity was strongly influenced by the structure of the N-protecting group X. By far the best results were obtained with X = tBuOCO [157].



44

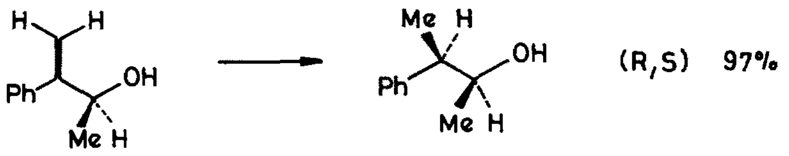
R = H, Me, $PhCH_2$
X = tBuOCO, Z, $CF_3CO$

Two analogs of leucine-enkephalin (a biologically active pentapeptide) were synthesized by the coupling of dipeptide and tripeptide units which both were obtained by the asymmetric hydrogenation of the corresponding dehydropeptides. $Rh(NBD)(L_2)^+$ complexes containing chiral diphosphines were used as catalysts [$L_2$ = diPAMP (7), Ph-CAPP (35)] [158]. Using the complex $[Rh(COD)(diPAMP)](BF_4)$ as catalyst (diPAMP = 7) the bisdehydropeptide (45) has been hydrogenated to the S,S-dipeptide with over 95% optical purity [159]. Diastereoselective hydrogenation of N-acetyl dehydro peptides was studied using $Rh(PPh_3)_3Cl$ [160].



45

Hydrogenation of the unsaturated alcohols (46) and (47) with $[Rh(NBD)(Ph_2PCH_2CH_2CH_2CH_2PPh_2)](BF_4)$ affords a high degree of stereoselection. The stereochemical course of the two reductions is opposite and can be rationalized by assuming a pseudo-equatorial conformation for the Me group in the intermediate $H_2Rh(olefin)(bisphosphine)^+$ complex [161]. The monosubstituted olefins styrene, tetramethylammonium propenoate and N-vinylacetamide were reduced with $D_2$ in the presence of chiral Rh-diphosphine complexes containing (-)-DIOP (1b), diPAMP (7) and chiraphos (38). No enantioselectivity was observed with styrene. Optical yields ranged between 11-51% for the other two substrates but the configurations of the



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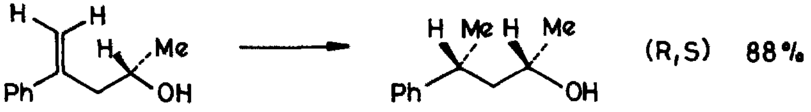
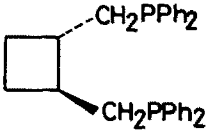
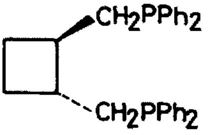


47

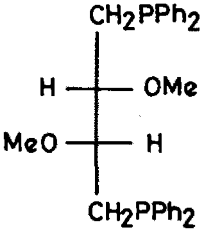
products did not correlate with those obtained with the same chiral ligands if α-acetamidoacrylic acid was reduced with $D_2$. Using HD as reductant a modest regioselectivity (1.36:1) in favor of the α-deuterated product was observed with (Z)-α-acetamidocinnamic acid as substrate [162]. Complexes generated in situ from HRh(CO)$(PPh_3)_3$, $Rh_6(CO)_{16}$ or $Rh_4(CO)_{12}$ and diphosphines are homogeneous catalysts for the hydrogenation of α,β-unsaturated aldehydes into saturated aldehydes. In the presence of the chiral phosphines (-)-DIOP (1b), (48), (49) and (50) neral and geranial are hydrogenated to citronellal with up to 71% optical yield [163].



(+)- 48



(-)- 48



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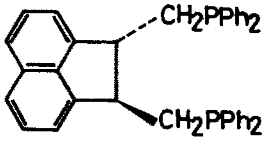


50

Asymmetric hydrogenation of 2-phenylbutene isomers to (S)-(+)-2-phenylbutane was accomplished with two catalytic systems: $Et_3Al$ + $Co(acac)_2$ + $P(nmen)Ph_2$ and $Et_3Al$ + bis(L-isoleucine)Co. The highest optical yield obtained with the former system was 25.8% [164].

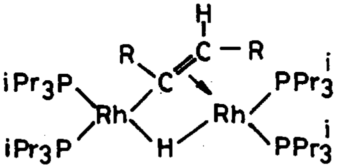
The reuse of Rh(I) complexes with ditertiary phosphines as ligands in the hydrogenation of 2-acetamidoacrylic acid has been investigated [165].

## 4. Hydrogenation of Dienes and Acetylenes

### a) Co, Rh and Ir Catalysts

Selective hydrogenation of nonbranched 1,3-diolefins mainly to cis-2-olefins was carried out in THF + EtOH with Co(bpy)$_2$X catalysts (X = Cl, Br, I) prepared in situ from CoX$_2$, bpy and Zn. Activity and selectivity of the catalysts depend on the time when butadiene and H$_2$ are introduced to the catalyst [166].

Toluene solutions of Rh$_4$(CO)$_{12}$ and Rh$_4$(CO)$_{12}$ anchored on $\gamma$-Al$_2$O$_3$ catalyze the hydrogenation of trans-1,3-pentadiene to 2-trans-pentene at 60-80°C and 1 bar H$_2$. Anchoring decreases the reaction rate but increases the stability of the catalyst which decomposes in solution after long reaction times to metallic Rh [167]. Alkynes are converted to trans olefins at 20°C and 1 bar H$_2$ by the dinuclear complex ($\mu$-H)$_2$Rh$_2$[P(OPr$^i$)$_3$]$_4$. The stereochemistry of H addition is governed by formation of the intermediate bridged vinyl complex (51) [168]:



51

Methanol solutions of the dinuclear cationic complexes Rh$_2$(CO)$_2$(Ph$_2$ECH$_2$EPh$_2$)$_2$($\mu$-X)$^+$ (X = Cl, Br; E = P, As) and Ir$_2$(CO)$_3$(Ph$_2$PCH$_2$PPh$_2$)$_2$Cl$^+$ are active catalysts for the hydrogenation of alkynes to alkenes, and alkenes to alkanes. Neutral complexes with pseudohalide ligands were also studied, but only the cyano-complex Rh$_2$(CO)$_2$(Ph$_2$PCH$_2$PPh$_2$)$_2$(CN)$_2$ and its arsine analog have significant catalytic activity [169]. A kinetic study of the reaction between HIr(CO)(PPh$_3$)$_3$ and H$_2$ or PhC$\equiv$CH provided evidence for the 14-electron intermediate HIr(CO)(PPh$_3$), as well as for a direct attack of H$_2$ on the 18-electron HIr(CO)(PPh$_3$)$_3$ [170].

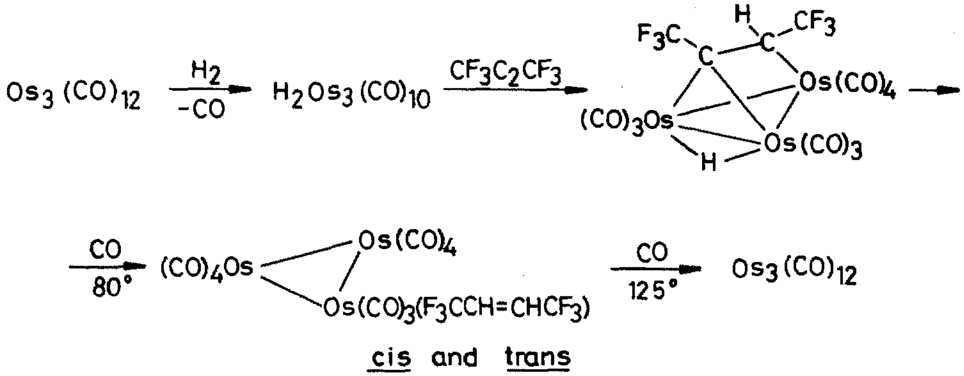
### b) Ni, Pd and Pt Catalysts

Cyclic diolefins were hydrogenated selectively to monoolefins with a catalyst prepared from Ni(acac)$_2$, $Et_3Al_2Cl_3$ and $PPh_3$ [171]. Amine complexes of palladium fixed on silica were prepared by reaction of $Na_2PdCl_4$ with silica containing (3-aminopropyl)silyl and [(3-aminopropyl)amino]silyl moieties. The first catalyst was characterized by monodentate and the second by bidentate binding of Pd. A highly selective catalyst for hydrogenation of 1-heptyne to 1-heptene was obtained by adding $Ph_3P$ to the bidentate Pd complex catalyst. The activity of both hydrogenation catalysts exceeded that of $Pd/SiO_2$ [172]. Two series of phosphines $PR_3$ (R = = $C_{10}H_{21}$ - $C_{19}H_{39}$) and $P(C_6H_4R^1\text{-}p)_3$ ($R^1$ = Et - $C_9H_{19}$) which form very soluble complexes, were used to prepare <u>cis</u>-[$PtL_2Cl_2$] and <u>trans</u>-[$PdL_2Cl_2$] complexes (L = $PR_3$, $P(C_6H_4R^1\text{-}p)_3$). The effect of the phosphines on the selective hydrogenation catalysts formed with $SnCl_2$ for polyunsaturated olefins was reported [173]. Some heteronuclear Pt clusters like $Pt_2Co_2(CO)_8(PPh_3)_2$ and $Pt(CNCy)_2[CpMo(CO)_3]_2$ catalyze the hydrogenation of terminal acetylenes to olefins and alkanes. The activity and selectivity of the catalysts is low. The Co-containing mixed cluster rearranges under the reaction conditions to $Pt_5(CO)_6(PPh_3)_4$ [174].

### c) Cr, Ru, Os, Cu and U Catalysts

The hydrogenation of α-terpinene and 2,3-dihydroanisole catalyzed by (phenanthrene)Cr(CO)$_3$ at 80°C and 7 bar $H_2$ has been described. Ketones accelerate the reaction [175]. The photochemical hydrogenation of NBD in the presence of $Cr(CO)_6$ yields nortrycyclene and nornbornene. Conjugated dienes give exclusively 1,4 hydrogenated products [176].

Divinylbenzene-styrene copolymers were diphenylphosphinated and complexed with $Ru(CO)_2(PPh_3)_2Cl_2$ to prepare a supported catalyst which gives 93.3% selectivity to cyclopentene in the hydrogenation of cyclopentadiene at 150°C compared with 97.4% selectivity for the unsupported complex [177]. A complete cycle of reactions has been described for the reduction of an alkyne to an alkene by $H_2$ in the presence of a metal cluster [178]:



The complex $Cu_2(OOCPh)_2(PhC_2Ph)$, formed from Cu(I) benzoate and diphenylacetylene absorbs $H_2$ at room temperature to yield 1,2-diphenylethane. The reaction is only stoichiometric even with an excess of $PhC_2Ph$ at 100°C and 50 bar [179].

The black reaction product obtained from the reaction between tBuLi and $UCl_4$ catalyzes the hydrogenation of alkenes and alkynes to alkanes at a slow rate at room temperature [180].

## 5. Hydrogenation of Arenes

Kinetic data were obtained for the hydrogenation of benzene and 15 mono- and disubstituted benzenes with $(\pi\text{-}C_3H_5)Co[P(OPr^i)_3]_3$ as catalyst and a linear Hammett plot was established. The rate determining step is either the addition of $H_2$ to the benzene-catalyst complex or a rearrangement within the benzene-catalyst-$H_2$ complex [181, 182, 183]. Rhodium complexes with amino acids catalyzed the hydrogenation of aromatic hydrocarbons, phenols and heterocyclic compounds [184]. Supported complexes prepared from $Rh_2(NBD)_2Cl_2$ and phosphinated polydiacetylene or silica $(SIL\text{-}CH_2CH_2CH_2PPh_2)$ are efficient catalysts for the hydrogenation of arenes at 30°C and 80 bar [185].

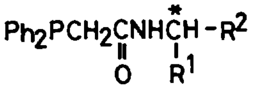
## 6. Hydrogenation of Carbonyl Compounds

$\alpha,\beta$-Unsaturated ketones are reduced by $HFe(CO)_4^-$ in THF to saturated alcohols. Isolated C=C double bonds or saturated ketones do not react [186]. The trinuclear cluster $(\mu\text{-}H)_2Ru_3(CO)_6(\mu\text{-}PPhCH_2PPh_2)$ catalyzes the hydrogenation of cyclohexanone to cyclohexanol at 90°C and 100 bar [187].

Hydrogenation of benzaldehyde is catalyzed by $Rh_6(CO)_{16}$ in MeOH solution at 110°C and 70 bar ($H_2$:CO = 4:1) in the presence of $NaHCO_3$ as base. The reaction is first order in PhCHO, 0.92 order in $Rh_6(CO)_{16}$ and is inhibited by CO. A detailed kinetic analysis supports a cluster catalytic mechanism. The slow step is a Rh-Rh bond cleavage resulting in a site of coordinative unsaturation where PhCHO bonds prior to hydrogenation [188]. Neutral Rh(I) hydride complexes $HRh(PR_3)_n$ (R = iPr, n = 3; R = Cy, n = 2) catalyze the reduction of ketones by $H_2$ or by transfer hydrogenation with iPrOH as H source. If fully alkylated diphosphines were used as ligands, the cationic Rh(I) complexes $[Rh(NBD)(P-P)](ClO_4)$ proved to be remarkably active [(P-P) = $iPr_2P(CH_2)_nPPr^i_2$, n = 3,4]. With these catalysts ketone hydrogenation was complete within minutes and also aldehydes could be hydrogenated without decarbonylation [189]. Benzaldehyde is hydrogenated at 40-80°C and 1.4-4.5 bar $H_2$ with $(NBu_4)([Pt_3(CO)_6]_5$ as catalyst precursor. Products are benzylalcohol (at lower pressure) or benzene and methanol (at higher pressures). The active catalyst is probably a Pt cluster as suggested by kinetic studies [190].

### a) Asymmetric Hydrogenation

The catalyst formed in situ from $Rh_2(NBD)_2Cl_4$ and (+)-DIOP (1a) catalyzes the hydrogenation of α-(N,N-dialkylamino)alkyl aryl ketones to give enantioselectivities of up to 95% [191]. Chiral, N-substituted diphenylphosphinoacetamides (53) and (54) were used as ligands in Rh(I) complex catalysts for hydrogenation of acetophenone and styrene in the presence of strong bases. The catalytic activity was enhanced significantly if a separate aqueous phase was present [192].



$Ph_2PCH_2\underset{O}{\underset{\|}{C}}NH\underset{R^1}{\underset{|}{\overset{*}{C}}}H-R^2$

$R^1$ = iPr, $PhCH_2$, Me

$R^2$ = $COOBu^t$, COOEt, Ph

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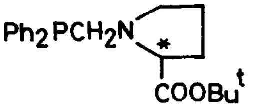

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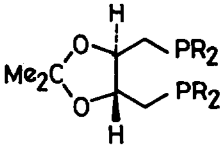
The tetraalkyl analogs of DIOP : (-)-EtDIOP (55), (-)-iPrDIOP (56) and (-)-CyDIOP (57) were prepared. Cationic Rh(I)complexes of these chiral ligands (P-P), $[Rh(NBD)(P-P)](ClO_4)$ proved to be highly active catalysts for asymmetric hydrogenation of ketones. In the hydrogenation of $PhCOCONHCH_2Ph$ 77% o.y. was achieved using (-)-CyDIOP [193,194].

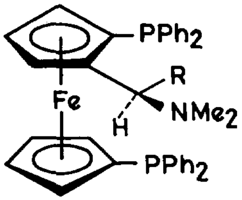


55, R = Et

56, R = iPr

57, R = Cy

The new ferrocenylphosphines (58) (R = $NR^1R^2$; $R^1$, $R^2$ = H, Me, Et, allyl, $Me_2NCH_2CH_2$, $MeNHCH_2CH_2$, $HOCH_2CH_2$; or $NR^1R^2$ = pyrrolidino, piperidino, 4-methyl-1-piperazinyl) were synthetized. The Rh complex of the ferrocenylphosphine (59 = BPPFOH) was an effective catalyst for asymmetric hydrogenation of prochiral carbonyl compounds (highest o.y. 95%) [195].



58, R see text

59, R = OH

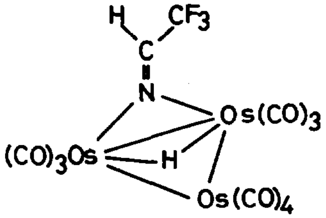
## 7. Hydrogenation of Nitro Compounds

$Co(dmg)_2$ and related Co(II) complexes catalyze the reduction of aromatic nitro compounds to give aromatic amines in 92-100% yield [196]. EPR spectra of dimorpholine cobaloxime and the rate of nitrobenzene hydrogenation catalyzed by this complex has been studied in different solvents. Catalytic activity varied videly whereas magnetic parameters showed no substantial variation with the solvent [197]. The complex $Pd_2(PPh_3)_2Cl_4$ was used as a homogeneous catalyst for the reduction of $PhNO_2$ and $p\text{-}ClC_6H_4NO_2$ with $H_2$ in basic EtOH. A reaction intermediate $Pd(PPh_3)(PhNO_2)Cl_2$ was isolated and characterized. Reduction of $PhNO_2$ produced 75% aniline, 5% azobenzene and 15% azoxybenzene under atmospheric pressure whereas under high pressure the reduction product contained aniline (95%) only [198]. Nitrobenzene hydrogenation and reductive alkylation with isobutanal were studied with catalysts formed from $K_2PdCl_4$, $K_3RhCl_6$, $K_2PtCl_6$, $K_3Fe(CN)_6$ and $K_3Co(NO_3)_6 \cdot 5H_2O$ complexed on anion exchange resins. The greatest activity was observed with Pd complexes on polytrimethylolmelamine [199].

## 8. Miscellaneous Hydrogenations

In the presence of $H_2$, methane can be a by-product in the carbonylation of MeOH to AcOH using iodine-promoted homogeneous

Rh catalysts. The $CH_4$ is formed by hydrogenolysis of MeOH [200]. Cationic Rh complexes of the type $[Rh(NBD)(PR_3)_2](ClO_4)$ catalyze the "abnormal" ring-opening hydrogenation of 3,4-epoxybut-1-ene to but-2-en-1-ol, the main product is, however, crotonaldehyde produced by isomerization [201]. The reaction of $CF_3CN$ with $H_2Os_3(CO)_{10}$ gives (60) and the treatment of this complex with $H_2$ at 49 bar and 140°C leads to the formation of (61), (62) and (63). These reactions suggest a model for the hydrogenation of a nitrile ligand [202].



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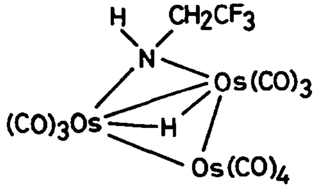

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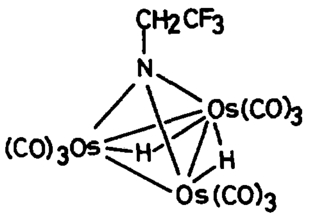

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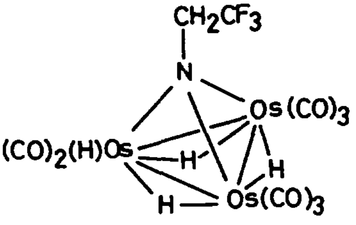

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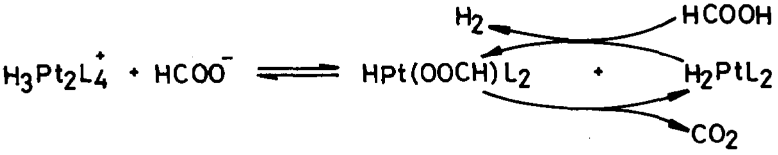
## 9. Dehydrogenations

The complexes $Ru(OOCCF_3)_2(CO)(PPh_3)_m(L-L)$ where (L-L) = 1,2-$(Ph_2P)_2C_6H_4$ (m = 0,1), $Ph_2PCH_2CH_2AsPh_2$ (m = 1) and $Ph_2P(CH_2)_nPPh_2$ (n = 3,4; m = 0) have been prepared and used as catalysts in alcohol dehydrogenation and ketone hydrogenation. These complexes are more active than $Rh(OOCCF_3)_2(CO)(PPh_3)_2$. All of them, however, deactivate by decarbonylation of the product aldehyde or ketone to form dicarbonyl complexes [203]. An immobilized Rh complex catalyst was prepared by reacting silica with $Ph_2P(CH_2)_2Si(OEt)_3$ and treating the phosphinated silica with $Rh_2(OAc)_4$. This catalyst was used for the dehydrogenation of iPrOH at 82°C in the liquid phase [204]. Photolysis decreases the activation energy of iPrOH dehydrogenation with $RhCl_3.3H_2O$ + $SnCl_2.2H_2O$ + LiCl homogeneous catalysts from 117 to 11 kJ $mol^{-1}$. The quantum efficiency exceeds unity in the u.v. region. The formation of catalytically active species by the photocleavage of Rh-Sn bonds is assumed [205].

Reaction of singly charged atomic Ni ions with n-butane in the gas phase yields $Ni(C_2H_4)_2^+$ via a 1,4 process. Ion cyclotron resonance studies suggest that loss of $H_2$ occurs by oxidative addition to the internal C,C-bond followed by a β-H transfer to the metal [206]. The decomposition of formic acid into $H_2$ and $CO_2$ is catalyzed by $H_3Pt_2(PEt_3)_4^+$ at 20°C in the presence of HCOONa [207]. Formato and hydrido complexes are the intermediates (L = $PEt_3$):



The cluster $(Bu_4N)_2[Fe_4S_4(SPh)_4]$ transfers electrons from PhLi to protons from PhSH in a homogeneous system, resulting in the generation of $H_2$ [208]:

$$2PhLi + 2PhSH \longrightarrow PhPh + H_2 + 2PhSLi$$

## 10. Hydrogen Transfer Reactions

### a) Alkanes as Hydrogen Donors

Cycloalkanes $C_nH_{2n}$ (n = 6,7,8) are dehydrogenated at ≤ 80°C to the corresponding cycloalkenes by $H_7Re(PAr_3)_2$ (Ar = $p\text{-}FC_6H_4$, $p\text{-}MeC_6H_4$, Ph) in the presence of 3,3-dimethylbutene as a H-acceptor [209]. The same system has been shown to transform n-pentane at 80°C to $H_3Re(\eta^4$-*trans*-penta-1,3-diene)$(PAr_3)_2$. $(MeO)_3P$ converts this complex with high selectivity to 1-pentene [210]. $H_2Ir(PPh_3)_2S_2^+$ (S = $H_2O$ or acetone) reacts with cyclooctane or cyclooctene in the presence of 3,3-dimethyl-1-butene to give $Ir(COD)(PPh_3)_2^+$. This system constitutes the first example of the dehydrogenation of an alkane by a transition metal complex which proceeds by a reverse-hydrogenation mechanism [211]. The coordinatively unsaturated $H_2Rh_2[P(OPr^i)_3]_4$ dehydrogenates 1,3-cyclohexadiene to benzene in a stoichiometric reaction, the other product is ($\eta^3$-cyclohexenyl)Rh $[P(OPr^i)_3]_2$ [211a].

Me groups bound to Rh in a complex are dehydrogenated to $\mu$-$CH_2$ groups by acetone and isopropanol is formed. Only certain H-acceptors are effective in this reaction [212].

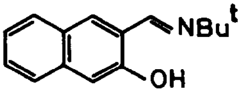
### b Hydrogenation of C=C Bonds

The complexes $[Rh(NBD)L_2](ClO_4)$ and $[Rh(NBD)L(PPh_3)](ClO_4)$, where L = substituted quinolines, catalyze the hydrogenation of olefins and the H-transfer from iPrOH to olefins and diolefins. No clear relation between the basicity of the quinoline ligand and the catalytic activity was found [213]. The rate of H-transfer from a secondary alcohol to an $\alpha,\beta$-unsaturated ketone, catalyzed by $HRh(PPh_3)_4$ depends on the order in which reactants are added to the catalyst. The hydroxylic H is regioselectively transfered to the $\alpha$-carbon of the ketone [214,215].

### c) Hydrogenation of C=O Bonds

The H-transfer reaction from iPrOH to cyclohexanones is catalyzed by Rh(III) and Ir(III) + $SnCl_2$ systems at 83°C. Ir was found to be the more active [216]. Ketones and olefins have been reduced at 83°C by H-transfer from iPrOH catalyzed by complexes formed <u>in situ</u> from $Rh_2(COD)_2Cl_2$ and various tertiary phosphines. $PCy_2Ph$ was found to yield the most active catalyst system. Reducing 4-t-butylcyclohexanone the <u>cis</u> alcohol is the favored product [217]. Methanol, cholesterol and citronellol are dehydrogenated to the corresponding carbonyl compounds in the presence of $Ru(PPh_3)_3Cl_2$ and cyclohexanone as a H acceptor at 140°C. Lactones are obtained from sugars under these conditions [218].

Supported complexes were prepared from $[Rh(NBD)_2](ClO_4)$ or Rh(NBD)L (where L = imidazole-ring containing ligand) and used as catalysts for the H-transfer reactions from iPrOH to acetophenone or 1-hexene [219]. Rh complexes catalyzed the H-transfer from $Me_2CHOH$ to cyclohexene or (less efficiently) to PhCOMe. The highest yields were obtained using $[MeORh(COD)]_2$ in the presence of (64) and (65) [220]:



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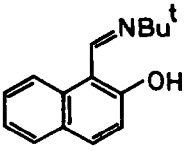

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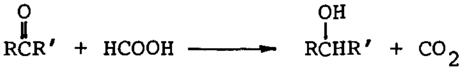
Ketones and aldehydes are reduced in good yields to alcohols by formic acid with $RuCl_2(PPh_3)_3$ as catalyst at 125°C. No solvent is necessary [221]:



$$R\overset{\overset{O}{\|}}{C}R' + HCOOH \longrightarrow R\overset{\overset{OH}{|}}{C}HR' + CO_2$$

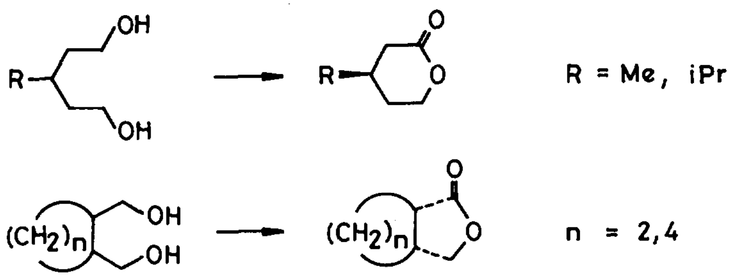
Both $HRh(CO)(PPh_3)_3$ and a catalyst made in situ from $RhCl_3.3H_2O$, $PPh_3$, and $Na_2CO_3$ catalyze the reaction of aldehydes with primary alcohols to give esters, together with alcohols formed by reduction of the aldehydes. The proportion of esters is increased by addition of an efficient H acceptor [222].

d) Asymmetric Hydrogen Transfer Reactions

In the H-transfer from chiral alcohols like (-)-2-exo,3-exo-camphandiol to acetophenone, catalyzed by $H_4Ru_4(CO)_8(PBu_3)_4$ a very slight enantioselection ( < 1%) has been observed. This suggests the simultaneous presence of the reagents in the catalytic intermediate [223].

H-transfer from racemic alcohols to prochiral ketones in the presence of $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ has been examined [(-)-DIOP = 1b]. Long reaction times were necessary and low optical yields were observed [224]. Asymmetric transfer hydrogenation of prochiral ketones by iPrOH using Ir complexes with chiral phosphines [(nmen)$PPh_2$, chiraphos (38), prophos (39) and (+)-DIOP (1a)] has been achieved. Best results (o.y. = 30%) were achieved in case of acetophenone and prophos [225].

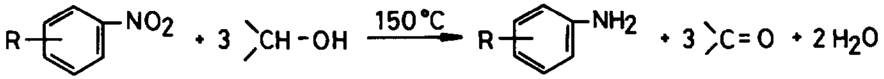
Enantioselective dehydrogenation of prochiral diols to lactones could be achieved by using $Rh_2[(-)\text{-DIOP}]_3Cl_4$ as catalyst and benzalacetone as H-acceptor [(-)-DIOP = 1b]. The catalyst was only active in the presence of $Et_3N$. Probably due to the high temperatures (110-150°C) optical yields were low ( < 15%) [226]:



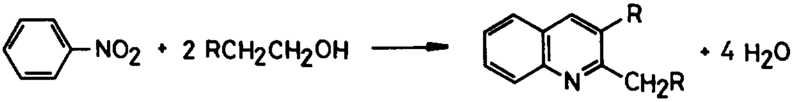
The disproportionation of aldehydes into acids and alcohols (Cannizzaro reaction) is catalyzed by phosphine-substituted derivatives of $H_4Ru_4(CO)_{12}$ in the presence of water. Using the (-)-DIOP (1b) substituted cluster a small asymmetric induction (1.7%) is observed in the formation of the acid [227].

e) Hydrogen Transfer to N or Halogen-containing Compounds

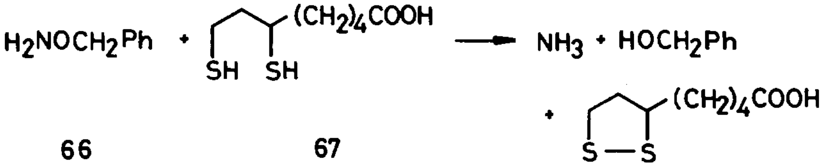
Aromatic nitro compounds were reduced by secondary alcohols like cyclohexanol to amines with Rh complexes as catalysts. Potassium acetate as a base was necessary for the reaction. The $PPh_3$/Rh ratio markedly influenced the catalytic rate, maximum activity was obtained at a ratio of 1/1 [228]:



Nitrobenzene reacts with ethanol and higher alcohols to form 2-Me- or 2,3-dialkylquinolines, respectively, in the presence of Rh and Mo complexes. The best yields are obtained with about equimolar mixtures of Rh and Mo at ≈ 180°C. The reaction mechanism probably involves dehydrogenation of the alcohols to aldehydes, reduction of nitrobenzene to aniline and successive condensations and aromatization [229]:



The N-O bond of hydroxylamine derivatives is reductively cleaved by dithiols in presence of Fe(II) to give the corresponding amines and alcohols (or water). The reaction between O-benzylhydroxylamine (66) and dihydrolipoic acid (67) has been investigated in detail [230]:



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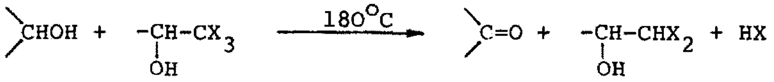
$Ru(PPh_3)_3Cl_2$ was shown to catalyze H-transfer from halogen-free alcohols to α-$X_3C$-carbinols and to give selectively dihalomethyl derivatives (X = Cl, Br). Since $\gamma$-trihalomethyl alcohols can be conveniently prepared from haloforms and aldehydes this catalysis is of synthetic value [231]:



$$>CHOH + -\underset{OH}{CH}-CX_3 \xrightarrow{180^{\circ}C} >C{=}O + -\underset{OH}{CH}-CHX_2 + HX$$

Aryl bromides and iodides are hydrodehalogenated by aqueous HCOONa under phase transfer conditions in presence of $Pd(PPh_3)_2Cl_2$ and $PPh_3$ (X = Br, I):

$$ArX + HCOONa \longrightarrow ArH + NaX + CO_2$$

Upon substitution of HCOONa by DCOONa in $D_2O$ the corresponding deuterated aryl compounds were obtained [232].

## 11. Reductions without Molecular Hydrogen

### a) Transition Metal Hydrides

Hydrozirconation of dienols, followed by acid hydrolysis, gave selectively alkenols with the double bond remote from the OH group intact. For example 1,7-octadien-3-ol treated with $Cp_2Zr(H)Cl$ in $C_6H_6$ at 10°C gave, after hydrolysis of the organozirconium complex with HCl, 1-octen-3-ol as the sole product in 69% yield [233]. $[(\eta^5-C_5Me_4Et)HTaCl_2]_2$ reduces MeCN to give a dinuclear complex containing the bridging NCHMe unit [234]. Ammonium-modified silica $SIL-(CH_2)_3-NEt_3.Cl^-$ and poly(styrene-divinylbenzene) resin incorporating ammonium groups Ⓟ$-CH_2-NEt_3.Cl^-$ were treated with a $CH_2Cl_2$ solution of $(HNEt_3)[HFe_3(CO)_{11}]$. Ion exchange supported the anionic clusters onto the functionalized solids. These products transformed nitrobenzene into aniline under mild conditions [235].

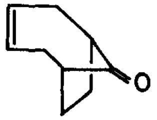
In the stoichiometric hydrogenation of $Ph_2C{=}CH_2$ by $HCo(CO)_4$ a CIDNP effect has been observed which proves that the reaction proceeds by a radical pair mechanism [236]. The rates of hydrogenation of several styrene derivatives by stoichiometric amounts of $HCo(CO)_4$ were measured and compared. The results support the previously proposed geminate radical pair mechanism [237]. Rate data for the stoichiometric radical hydrogenation of four conjugated aromatic olefins with $HCo(CO)_4$, $DCo(CO)_4$, $HMn(CO)_5$ and $DMn(CO)_5$ show, that these reactions proceed by similar mechanisms. The kinetic isotope effect varied from 0.43 to 2.02 and the rates were found to be two orders of magnitude slower for the Mn complexes than the Co complexes

[238]. $Ph_3COH$ is hydrogenated by $HCo(CO)_4$ quantitatively to $Ph_3CH$, catalytic quantities of $HBF_4.Et_2O$ increase the rate by a factor of more than 1000. $Ph_3C^+$ and $Ph_3C\cdot$ were proposed as intermediates [239].

A marked inverse kinetic isotope effect has been observed for the hydrogenation of NBD by $H_2Ir(PPh_3)_2(Me_2CO)_3^+$ and its $D_2$ analogue [240].

b) Low Valent Transition Metal Complexes

Reduction of bicyclo [4.2.1]non-3-en-9-one (68) by Ti(II) gave mostly the expected diastereoisomeric pair of alcohols, but reduction by Ti(O) gave in addition olefinic, saturated and partially saturated olefinic dimers and pinacol dimers [241]. In the reaction of $Cp_2Ti(CO)_2$ with phtalazine (69) electron transfer from Ti to the organic ligands leads to a radical species which may dimerize or abstract H atoms from the THF solvent to give complex (70). This type of reduction is important in the radical chemistry associated with coal liquefaction [242].



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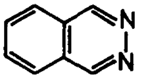

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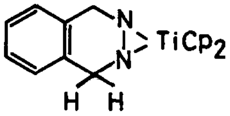

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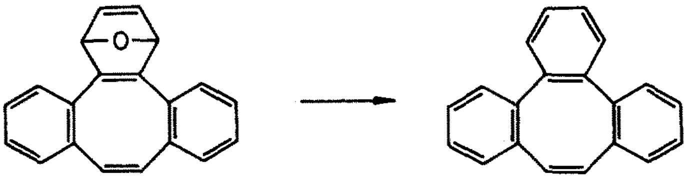
Benzhydrols, $R_2CHOH$ (R = Ph, p-tolyl, p-anisyl, $4-ClC_6H_4$) were reduced in mesitylene containing PhCOCl and $Fe(CO)_5$ to yield the respective diphenylmethanes and 1,1,2,2-tetraphenylethanes. Similarly the compounds PhC(OH)RR' (R = Ph, p-tolyl, p-anisyl, $4-ClC_6H_4$; R' = H, p-anisyl, $4-ClC_6H_4$) were converted to $PhCHRR^1$ [243]. The nature of the complex reducing agents prepared from Ni or Zn salts, NaH and a tertiary alcohol abbreviated as NiCRA and ZnCRA, respectively has been investigated in detail. It appears that the metal is formally in a zero-valent oxidation state in both reagents [244].

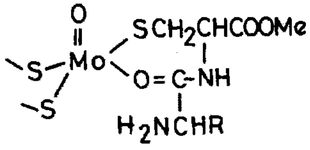
c) Inorganic Reductants in the Presence of Transition Metal Complexes

The hydrogenation of olefins by $LiAlH_4$ is catalyzed by $UCl_3$ dissolved in THF [245]. Deoxygenation of 7-oxabicyclo [2.2.1] hepta--2.5-diene systems like (71) to substituted benzenes was achieved by the use of $TiCl_4$ + $LiAlH_4$ [246]:



71

Complexes of the type $Mo_2O_2(\mu\text{-}S)_2$(cys-containing-dipeptide$)_2$ (72) and (73) catalyze the reduction of azobenzene to hydrazobenzene by $NaBH_4$ in protic media. Analogous complexes (74) having a 5-membered chelation of the cysteine residue were inactive [247].



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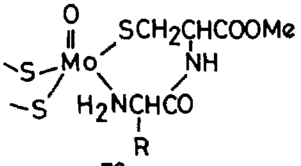

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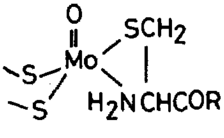


74

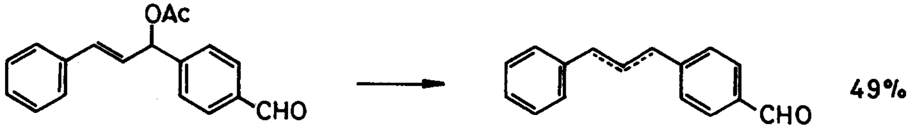
The combination of Co(II) halides with $NaBH_4$ has been frequently employed to reduce functional groups which are inert to $NaBH_4$ alone. It has recently been found that if used to reduce nitriles to amines, cobalt boride ($Co_2B$) is formed which coordinates to the nitrile and catalyzes its heterogeneous reduction by $NaBH_4$. In accordance with this, $tBuNH_2.BH_3$, a reagent inert to nitriles could be used to reduce benzonitrile in the presence of $Co_2B$ [248]. $NaBH_4$ + $RhCl_4$ + $RhCl_3.3H_2O$ in EtOH reduce aromatic nuclei to the corresponding saturated cyclic compounds at 30-40°C. The reaction is stoichiometric and the preincubation of the aromatic substrates with rhodium chloride before addition of $NaBH_4$ is essential for the reduction [249]. Hydride can be added to dicationic ($\eta^6$-benzene complexes like ($\eta^5$-$C_5Me_5$)M($\eta^6$-$C_6H_6$$)_4^{2+}$ (M = Rh,Ir) or ($\eta^6$-$C_6H_6$$)_2Ru^{2+}$ to give the corresponding $\eta^4$-cyclohexadiene complexes. In the presence of benzene the initial $\eta^6$-benzene complexes can be regenerated by $BF_3.2H_2O$ and cyclohexene is liberated (yields 60-94%). This represents a cycle where benzene is hydrogenated to cyclohexene by first adding two hydrides and then two protons and which is catalytic in the platinum metal complex [250].

Triisobutylaluminium reduces $\alpha,\beta$-unsaturated ketones to saturated ketones in the presence of catalytic amounts of bis (N-methylsalicylaldimine)Ni. A Ni hydride species is regarded as the active catalyst. The complex [(-)-DIOP]$NiCl_2$ [(-)-DIOP = (1b)] is not effective in this reduction [251]. The C=C bond is reduced in α, β-unsaturated carbonyl compounds by $Bu_3SnH$ in the presence of $Pd(PPh_3)_4$ with almost complete chemoselectivity if a radical scavenger is added. The results suggest $Bu_3SnH$ to act as a hydride donor [252]. Acetic acid or $ZnCl_2$ promote the reduction of α, β-unsaturated carbonyl compounds by $Bu_3SnH$ catalyzed by $Pd(PPh_3)_4$. Proton donors (acetic acid, p-nitrophenol) also promote the hydrogenolysis of alkyl aryl ethers (75) and allyl carbamates (76) with $Bu_3SnH$ [253]:

75

76

Allylic acetates (like 77) and allylic amines (like 78) can be reductively cleaved by $Bu_3SnH$ in the presence of $Pd(PPh_3)_4$. The reaction is highly chemoselective, other functional groups like aldehydes and nitriles are unaffected [254]:



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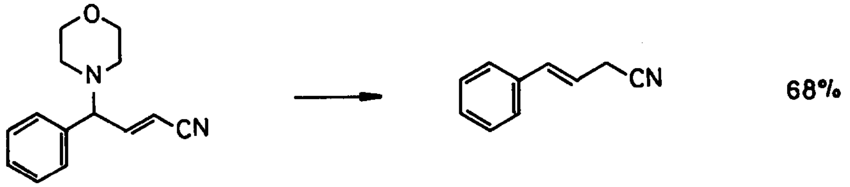


78

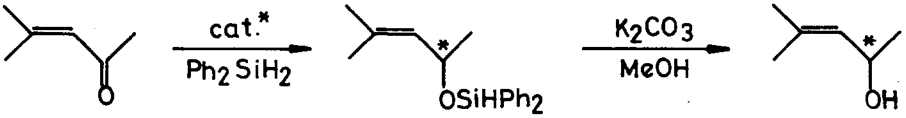
The combination of $Pd(PPh_3)_4$ and $LiBHEt_3$ provides an effective system for the reductive removal of allylic functional groups like ethers, sulfides, sulfones, selenides and silyl ethers [255]:

X = OMe, OPh, SPh, $SO_2Ph$, SePh, $OSiMe_2Bu^t$

### d) Reduction of Carbonyl Compounds via Hydrosilylation

4-tert-Butylcyclohexanone reacts with $Et_3SiH$ in high yield to provide predominantly (up to 95%) the more stable equatorial silyl ether in the presence of $Rh(PPh_3)_3Cl$ or $Ru(PPh_3)_2Cl_2/CF_3COOAg$. After hydrolysis, the corresponding alcohols are obtained [256]. Highly regioselective reduction of α, β -unsaturated carbonyl compounds giving the corresponding saturated carbonyls or allylic alcohols was effected by hydrosilylation catalyzed by $Rh(PPh_3)_3Cl$ followed by methanolysis of the resulting adducts. In general, monohydrosilanes afforded saturated carbonyl compounds while dihydrosilanes gave allyl alcohols [257].

Regioselective asymmetric reduction of prochiral α, β -unsaturated ketones (e.g. 79) to optically active allyl alcohols was performed via hydrosilylation catalyzed by Rh(I) complexes with (+)-BPPM (37a), (+)- and (-)-DIOP (1a and 1b) as chiral ligands. Optical yields up to 69% were achieved [258]:



Steroid 17-ketones were reduced to the corresponding alcohols by hydrosilylation with a hydrosilane ($Ph_2SiH_2$, $Ph_3SiH$, $n$-$C_5H_{11}SiH_3$) in presence of the chiral Rh complex generated in situ from $Rh_2(COD)_2Cl_2$ and (+)- or (-)-DIOP (1a or 1b) followed by hydrolyzing the resulting silyl ethers. In certain cases relatively high yields of α-alcohols were obtained [259].

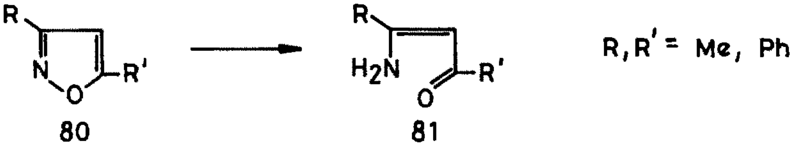
### e) Organic Reductants in the Presence of Transition Metal Complexes

In the presence of $(Et_2NCS_2)_2MoO$ as catalyst at 40-80°C $Ph_3P$ deoxygenates compounds containing heteroatom-O bonds like $Ph_3PAsO$, $Me_2SO$ and pyridine N-oxide [260]. The reduction of p-nitrobenzylchloride to p-nitrotoluene by ascorbic acid is catalyzed by Fe(TPP)Cl in the presence of a phase transfer agent. The complex (TPP)Fe-$CH_2C_6H_4NO_2$-p is formed as an intermediate [261].

### f) Photochemically Assisted Reductions

3,5-Disubstituted isoxazole derivatives (80) when irradiated in the presence of $Fe(CO)_5$ and $H_2O$ (in a moist solvent containing an equivalent amount of water) undergo reductive cleavage of the

N-O bond to give β-aminoenones (81) in good yields. The same reaction may be performed by $Fe_2(CO)_9$ under thermal conditions (50°C) [262]:



Irradiation of $H_4Ru_4(CO)_{12}$ or $H_2Ru_4(CO)_{13}$ in the presence of olefins effects their stoichiometric hydrogenation at 25°C [263]. Photo-induced electron transfer from $Cu^+$ to electronically excited 10-Me-acridinium tetrafluoroborate in MeCN + $H_2O$ solutions leads to $Cu^{2+}$ and 10,10'-$Me_2$-9,9'-biacridane [264].

The photochemical reduction of methylviologen (MV) was sensitized by $Ru(byp)_3^{2+}$ complexes bound to polystyrene beads with a polyoxyethylene spacer group [265]. The MV radical cation was detected by conventional resonance Raman spectroscopy in photoreductions of MV with monoprotonated proflavin or $Ru(byp)_3^{2+}$ as sensitizers [266]. The photosensitized reduction of MV and dissolved $O_2$ with the aid of triethanolamine as a donor by $Ru(byp)_3^{2+}$ adsorbed in a network of a water-swollen cation exchange resin has been studied. $H_2O_2$ is produced via $O_2^-$, which is formed by the reaction of the MV radical with $O_2$ [267].

### g) Electroreductions

The electroreduction of $CO_2$ was catalyzed by the iron-sulfur clusters $[Fe_4S_4(SR)_4]^{2-}$ (R = $PhCH_2$, Ph). Formate was obtained preferentially, but considerable amounts of hydrocarbons (mainly $C_3$) were detected too [268]. The catalytic reduction of MeNC (to $MeNH_2$ and $CH_4$) and MeCN (to $C_2H_6$ and $NH_3$) has been carried out under controlled potential electrolysis with a Hg working electrode in the presence of $[Fe_4S_4(SPh_4)]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ [269]. The reduction of gem. dibromocyclopropanes with electrochemically generated Cr(II) was studied [270]. The electrochemical reduction of deoxybenzoin with Cr salts in DMF leads primarily to hydrodimerization of the glycol. The chemical reduction by chromous salts is too slow to be of interest [271].

# IV. Oxidation

## 1. Catalytic Oxidation of Hydrocarbons with $O_2$

### a) General

Reaction rate pulsation has been observed during liquid-phase oxidation of hydrocarbons (p-xylene and dodecane) by $O_2$ in the presence of Co(II), Mn(II), Cr(III) or Fe(III) salts as catalysts [272]. The satbility constants and ΔH values of Co(II) complexes with alkylpyridines, pyridinecarboxaldehydes , and pyridinecarboxylic acids were determined. Reactivities in alkylpyridine + $Co(II)^+Br^-$ oxidation systems could be explained on the basis of the conversion of active Co(II)-alkylpyridine complexes into inactive complexes of Co(II) with the O-containing products [273].

### b) Oxidation of Alkanes

n-Pentadecane oxidation was carried out with stearates of Cr(III), Fe(III), V(II), Mo(II), Co(II) and Mn(II) or their mixtures as catalysts. The effect of catalyst nature on product composition was studied [274]. 15 Three-component stearate catalysts (Al, Ce, Co, Cr, Cu, Pb, Mn, Ni, K, Na) for the oxidation of pentadecane were examined. The most selective ones for formation of acids were Mn-Ni-K and Mn-Ce-K [275]. The effect of several transition metal ions on the liquid-phase air oxidation of n-pentane at 165°C and 50 bar was investigated. Fe and Ni ions increased the yield of AcOH, Cr ions increased the yields of AcOH and EtCOOH and Nb ions increased the yield of HCOOH [276].

The liquid phase oxidation of pentadecane gave ketones with 70% selectivity at 120°C in the presence of $Cr(st)_3$ + $Ni(st)_2$ as catalyst [277]. $Mn(OAc)_2$ (30-35% aqueous solution) increased the yield and selectivity for HCOOH and decreased those for $Me_2CO$ during the oxidation of a pentane fraction and of hexane with $O_2$ without affecting the AcOH and EtCOOH yields significantly [278]. Catalysts containing $CpMn(CO)_3$, ( $\eta^5$-$C_5H_4COOH)Mn(CO)_3$, $Mn_2(CO)_{10}$ or $Mn(st)_2$, $Ni(st)_2$, and either Na(st) or K(st) oxidized alkanes to carboxylic acids, those containing 1:0.5:1.3 = Mn:Ni:K being the most active. Neutral, O-containing byproducts are also formed which slow down the reaction owing to complexation with the catalyst [279]. Liquid-phase oxidation of isobutane was examined with Mn, Cr and Fe acetates as catalysts and without any catalyst. Mn acetate increased the selectivity for acetone but a lower conversion of isobutane was obtained in this case [280].

Fe and Mn phthalocyanine complexes on polystyrene were prepared and characterized by ESR, transmittance electron microscopy, scanning electron microprobe analysis, and DSC. The catalytic activity in oxidation of cyclohexane was somewhat higher than that of nonsupported phthalocyanines [281]. Oxygenation reactions of adamantanes with $Fe^{2+}$+ $O_2$ in aqueous phosphate buffer solution were investigated. The oxy-functionalization of adamantane-1-acetic acid and adamantane-1-carboxylic acid is quantitative [282]. Selective oxidation of cyclohexane by $O_2$ to cyclohexanol and cyclohexanone was studied. The catalytic activity of Fe(TPP)Cl, Co(TPP), Mn(TPP)Cl and Cu(TPP) in presence of ascorbic acid was compared with that of natural hemin, which was the most active [283]. Hemin catalyzes the selective oxidation of cyclohexane to cyclohexanol and cyclohexanone in the presence of ascorbic acid. Of the metalloporphyrins studied Fe(TPP) showed catalytic activity comparable to that of hemin [284].

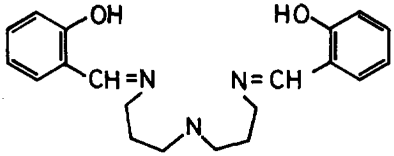
The effect of cobalt naphthenate on hydroperoxide accumulation in cyclododecane and phenylcyclohexane oxidation was investigated [285]. Addition of Co naphthenate in the oxidation of cyclohexane lowered the yield of adipic anhydride and increased the yield of adipic acid [286]. A mechanism for the oxidation of cyclohexane in HOAc with $O_2$ catalyzed by $Co(OAc)_2.4H_2O$ at 80-95°C to give adipic acid was proposed. This involves the formation of a cation radical species through the interaction of $Co^{3+}$ and cyclohexane as the rate-determining step [287].

### c) Oxidation of Olefins

Of the 12 acetylacetonate chelates examined $Co(acac)_2$, $Mn(acac)_2$ and $Mn(acac)_3$ were the most active catalysts for the oxidation of Me oleate and linoleate [288]. The catalytic activity of $[Co_3O(OAc)_6(HOAc)_3]$, $[Mn_3O(OAc)_6(HOAc)_3]OAc$ and $[Ru_3O(OAc)_6(H_2O)_3]OAc$ in the liquid-phase oxidation of 1-acetoxyhexene decreased in the order stated. However, the Ru complex was the most effective in the addition of peroxy radicals to the C=C bond [289].

The kinetics of 1-decene oxidation were studied with metal acetylacetonate catalysts and azoisobutyronitrile (AIBN) as initiator. In the absence of AIBN no induction period was observed with $Co(acac)_2$, $Cr(acac)_2$, $Ni(acac)_2$ or $Cu(acac)_2$. Induction periods occured with alkali- and alkaliearth metal complexes [290]. The

Co(II) complex of (82) catalyzes the oxidation of terminal olefins to ketones and sec-alcohols. The reaction is not a free radical initiated autoxidation. Synergistic enhancement of the reaction rate with the addition of $Rh(PPh_3)_3Cl$ has been observed [291].



82

The hydride $HIrCl_2(COD)(DMA)$ (DMA = dimethylacetamide) catalyzes the co-oxidation of cyclooctene and $H_2$ to cyclooctanone and $H_2O$:

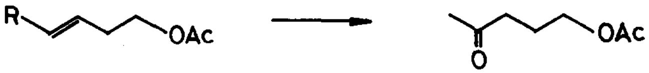
$$C_8H_{14} + O_2 + H_2 \longrightarrow C_8H_{14}O + H_2O$$

No oxygenation of cyclooctene occurs in the absence of $H_2$ and the reaction is not a free-radical autoxidation. An Ir(III) hydroperoxide is a likely intermediate [292].

$PdCl_2$ catalyzed the isomerization of 1-heptene to *cis*- and *trans*-2- and 3-heptene during oxidation to 2-heptanone and gave significant yields of 3- and 4-heptanone as impurities. Conditions for obtaining highest selectivities for each isomer heptanone were determined [293]. Using the $PdCl_2$ + $CuCl_2$ catalyst system internal olefins with an allylic alkoxy or acetoxy group were regioselectively oxidized with $O_2$ to form the corresponding β-alkoxy or β-acetoxy ketones:

R = alkyl
R′ = alkyl, Ac

Similarly, γ-acetoxy ketones were obtained from homoallyl acetates having an internal double bond [294]:

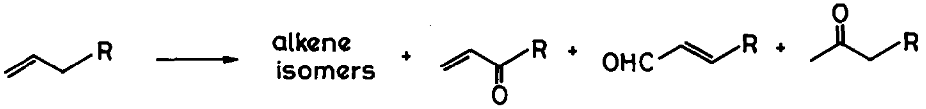


γ-Keto esters and 1,4-diketones were prepared by the regioselective oxidation of α,β-unsaturated esters and ketones with $O_2$ using the $PdCl_2$ + $CuCl_2$ catalyst system in aqueous dioxane [295]:

R = alkyl

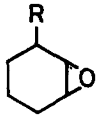
X = alkyl, OR

The oxidation of deuterated allyl alcohol $CH_2=CHCD_2OH$ by $PdCl_2$ was studied. The product composition suggests that it is the hydroxypalladation of the olefin which is the slow step of the Wacker-oxidation [296]. In the Pd-complex catalyzed oxidation of $C_2H_4$ in HOAc, the decomposition of the intermediate $[XX'Pd(Nu)-CH_2CH_2OAc]^-$ (X, X' = Cl, AcO; Nu = $O_2$, ONO, Cl, AcO) determines the reaction products. Increasing the positive charge on Pd a hydride shift becomes more favorable and $AcOCH=CH_2$ or $MeCH(OAc)_2$ is formed. With the electron density on Pd increasing the reaction with a $H_2O$ molecule to form $HOCH_2CH_2OAc$ becomes more likely [297]. Oxidation of butadiene in alcohol solutions of Pd(II) and Cu(II) halides gave $ROCH_2CH(OR)CH=CH_2$ and $ROCH_2CH=CHCH_2OR$ (R = alkyl)[298]. Irradiation of α-olefins in anhydrous solvents in the presence of $Pd(OOCCF_3)_2$ under $O_2$ leads to isomerized alkene, methyl ketones and α,β-unsaturated carbonyl compounds [299]:



d) Epoxidation of Olefins

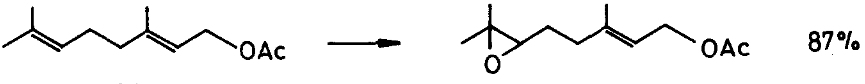
The main products of the liquid phase epoxidation of cyclohexene by $O_2$ or 2-cyclohexen-1-yl hydroperoxide catalyzed by $VO(acac)_2$ were 2-cyclohexen-1-ol and the epoxides (83). The formation of (83b) proceeds mainly by intramolecular rearrangement of 2-cyclohexen-1-yl hydroperoxide [300, 301a].



83 a, R = H

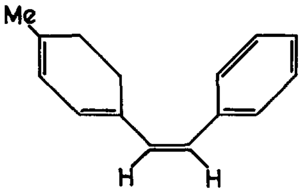
83 b, R = OH

The epoxidation of olefinic alcohol acetates like geranyl acetate (84) by $O_2$ is catalyzed by $[Fe_3O(OOCCMe_3)_6(MeOH)_3]Cl$ at 60°C. Oxygen is required in twice the ideal stoichiometry because one O atom is used for epoxidation and the other O atom is consumed in oxidative degradation of the substrate [302].



84

The $Ru(byp)_3^{2+}$ sensitized photooxidation of cis-stilbenes like (85) by $O_2$ in MeCN gave epoxides, the usual [2+4], and the novel [2+6] cycloadducts (see e.g. (86), (87) and (88), respectively) [302a].



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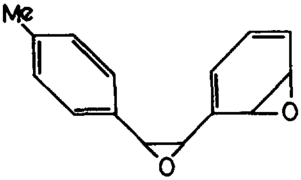

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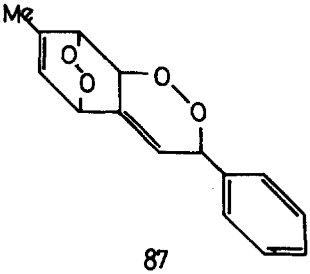

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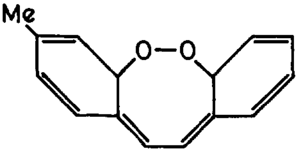

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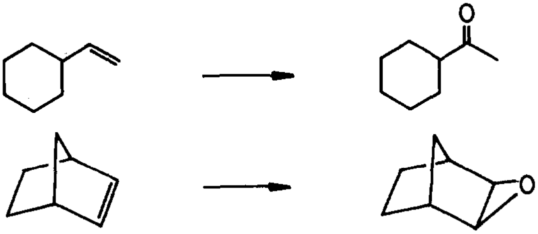
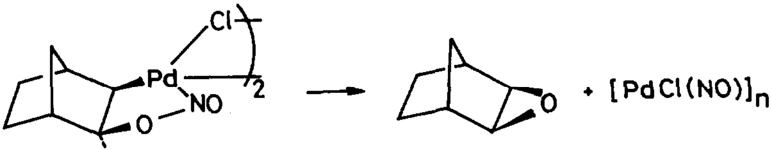
Vinylcyclohexane and some derivatives are oxidized to methylketones, norbornene and its derivatives are epoxidized by $O_2$ in presence of $PdCl(NO_2)(NCMe)_2$ [303]:



Reaction of $Pd(MeCN)_2Cl(NO_2)$ with norbornene leads to the quantitative formation of metallacycle (89) which slowly decomposes to exo-epoxynorbornene (90):



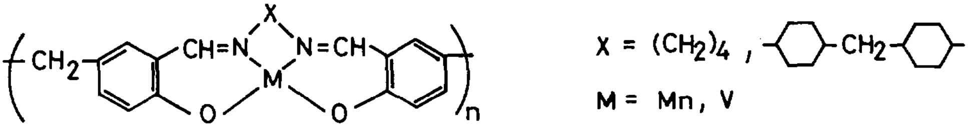
89

90

In the presence of air this epoxidation becomes catalytic. Other cyclic olefins react similarly [304].

### e) Oxidation of Aromatic Hydrocarbons

$H_6PW_9V_3O_{40}$, $H_7SeW_9V_3O_{40}$ and $H_7SiMo(VI)_9Mo(V)_3O_{40}$ catalyzed the liquid-phase oxidation of 1,2,3,4-tetrahydronaphthalene to form hydroperoxide, alcohol, and ketone [305]. Polymeric Schiff-base complexes of V(II) and Mn(II) (91) take up $O_2$ reversibly and catalyze the oxidation of cumene to 2-phenyl-2-propanol and acetophenone [306].



91

The oxidation of aromatic compounds by $O_2$ in the presence of the Fe(II)+EDTA+ascorbic acid system is improved by metallic iron powder, which serves to eliminate oxalic acid. This byproduct displaces EDTA and inhibits the selective hydroxylation [307].

Fixed Co catalysts were prepared by treatment of silica and lithiated silica with $CoCl_2$ or $Co(acac)_2$. The activity, selectivity and stability of the lithiated fixed catalysts in tetralin oxidation exceeded those of $CoCl_2$-impregnated silica [308]. Kinetic studies of p-xylene oxidation with a $Co^{2+}$ + $Mn^{2+}$ + $Br^-$ catalyst suggests that the active catalytic species is a complex containing $Co^{2+}$, $Mn^{2+}$, $Br^-$, p-xylene, and reaction intermediates [309]. The oxidation of a mixture of p-xylene and p-toluic acid to terephtalic acid by air and catalyzed by Co or Mn salts has been performed in water as solvent at 180-190°C with high yields [310]. $ROC_6H_4CHO$ [R = alkyl, cycloalkyl, (un)substituted Ph] were prepared by liquid-phase oxidation of $ROC_6H_4Me$ with $O_2$ in HOAc in the presence of $Co(OAc)_2$ and NaBr [311].

The kinetics of anthracene oxidation to anthraquinone by $O_2$ in presence of $Cu_2(OAc)_4$ and LiCl in AcOH was determined [312]. The initial rates in the oxidation of anthracene with $O_2$ at 90°C by use of Cu(II) chloro complexes in a mixture of acetic acid and $H_2O$ were studied. The rates of consumption of anthracene and $O_2$ are approximately equal and can be described by the following rate law [313]:

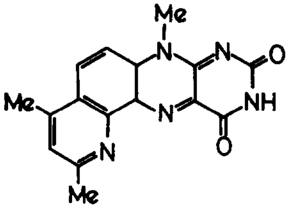
$$\frac{-d[A]}{dt} = [A][Cu_2(OAc)_4]^{0.5-0}[NaCl]^{1-0} \quad (A = \text{anthracene or } O_2)$$

ESR and IR studies show that during the oxidation of cumene with a Cu(II) + AN 251 anion exchange resin catalyst the structure of the catalyst is significantly changed: the Me group of the 2-Me-vinylpyridine moiety is oxidized to give an α-picolinic acid fragment thus altering the coordination sphere of Cu(II) [314]. Cu(II) and Mg compounds display synergism in catalyzing the oxidation of PhEt [315].

## 2. Catalytic Oxidation of O-containing Functional Groups with $O_2$

### a) Oxidation of Alcohols

The $Zr^{4+}$ complex of the flavin (92) oxidizes alcohols to carbonyl compounds at 30°C. In the presence of $O_2$ it acts as an oxidation catalyst for the same reaction, $H_2O_2$ is formed as byproduct [316]. Solutions of $PW_{12}O_{40}^{3-}$ catalyze the photooxidation of isopropyl alcohol to acetone by $O_2$ [317].

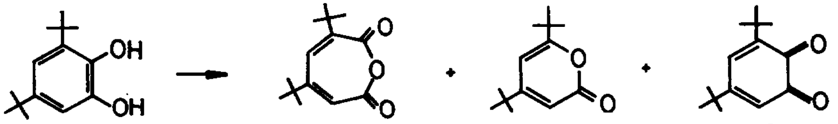


92

Primary alcohols were oxidized by $O_2$ to carboxylic acids in aqueous-alkaline solutions containing a Cu-phen complex. The reactivity of alcohols increased in the following order: MeOH < EtOH < PrOH < $Me_2CHCH_2OH$ < BuOH [318]. Cyclohexanol is oxidized by the same catalyst at 60-100°C and 2-4 bar $O_2$ [319]. The catalytic activity of Cu phthalocyanine increased during vapor-phase oxidation of MeOH owing to thermolysis of the complex in $O_2$ [320].

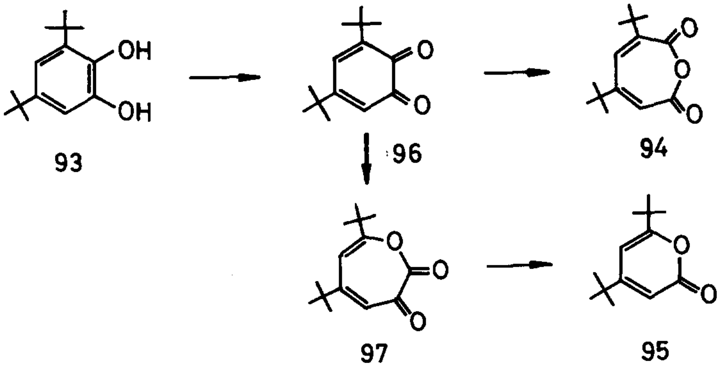
### b) Oxidation of Phenols

Oxygenation of (93) to the corresponding muconic anhydride (94) and 2-pyrone (95) is efficiently catalyzed by vanadium (III or IV) complexes like $VO(acac)_2$ or VCl(salen) at 20°C. The quinone (96) can not be oxidized under these conditions [321]:

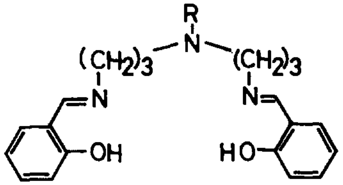


93 94 95 96

Oxidation of the catechol (93) with $O_2$ and $Ru(PPh_3)_3Cl_2$ as catalyst also yields (94) and (95). In this case, however, (96) and (97) were shown to be the intermediates [322]:



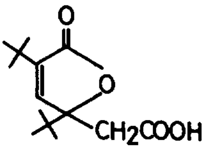
The monomeric (98) and the polymer-attached (99,Ⓟ = chloromethylated polystyrene resin) Schiff-base complexes of Co(II) were found to be about equally active in catalyzing the oxidation of 2,6-di-t-butylphenol by $O_2$ to the corresponding quinone [323].



98, R = Me

99, R = Ⓟ - $-CH_2-$

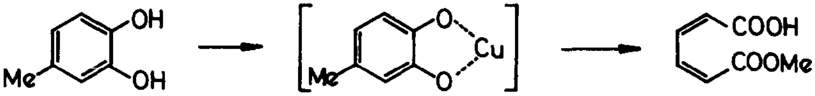
The oxidation kinetics of hydroquinone by $O_2$ were studied in aqueous solutions containing $Fe^{2+}$ at 30-50°C. The reaction is second order in hydroquinone and zero order in $Fe^{2+}$. The rate-limiting step is the electron transfer from $Fe^{2+}$ to $O_2$ [324]. The oxidation of 3,5-di-t-butylcatechol (93) to (96) and (100) by $O_2$ is catalyzed by $FeCl_2$ in presence of N bases. The yield of the $O_2$-inserted product (100) is highest when py and phen together are used as N ligands [325].



100

The $FeCl_3$-catalyzed oxidation of (93) to 3,5-di-t-butylquinone (96) by $O_2$ in THF was significantly promoted by addition of $SiO_2$, $\gamma$-$Al_2O_3$ and active carbon in situ [326]. Photo-oxidation of aryl ethers by air in the presence of $FeCl_3$ in aqueous MeCN afforded alcohols, aldehydes (or ketones), and N-alkylacetamides [327].

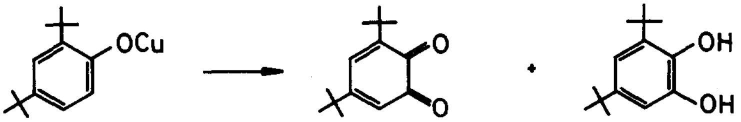
Kinetic data indicate that the oxidation of 3,5-di-tBu-catechol (93) to the corresponding quinone (96) in the presence of $Cu^{2+}$ proceeds via a 1:1 complex of $Cu^{2+}$ and the catechol [328]. The complex (phen)(3-n-nonylcatecholato)Cu reacts with $O_2$ to give 2-n-nonylmuconic acid and several secondary oxidation products [329]. The complex obtained from CuCl in py/MeOH and $O_2$ oxidatively cleaves 4-Me-catechol to Me-muconic acid Me-ester. The kinetics of the reaction suggests a complex of type (101) as the intermediate:



101

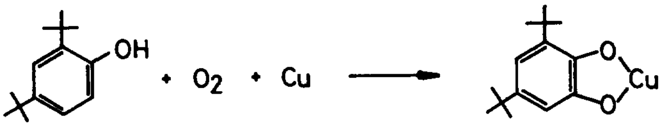
A Cu complex bound to a poly(styrene-co-4-vinylpyridine) was also found to be effective [330]. The oxidation of hydroquinone to quinone by $O_2$ was investigated in the presence of CuCl, $CuSO_4$, $Cu(OAc)_2$, $FeCl_3$ and different heterogeneous catalysts. Among the transition metal salts examined, CuCl was the most effective [331]. Crosslinked chelating resins with hydrazide or polyethylenepolyamine side chains were prepared and the catalytic activity of resin-metal chelates for the oxidation of 2,6-dihydroxyphenylacetic acid and hydroquinone by air investigated. Macroreticular resin - Cu(II) chelates were found to be suitable catalysts and could be used repeatedly [332].

The oxidation of cuprous phenoxides like (102) by $O_2$ leads to o-benzoquinones (96) and catechols (93) (the latter being present partly in the form of their Cu(II)-chelates) [333]:



102 96 93

Cyclic Cu(II) catecholates (103) are formed also by the oxidation of phenols and stoichiometric amounts of metallic copper with $O_2$ in the presence of CuCl as catalyst [334]:


103

ArCu and $Ar_2CuLi$ complexes are oxidized by $O_2$ at 0°C mainly to the corresponding phenols (and not biphenyls) if the Ar group contains alkoxy groups in the ortho position [335].

### c) Oxidation of Aldehydes and Ketones

The oxidation of propionaldehyde with $O_2$ in the presence of Co tetra(p-tolyl)porphyrin as catalyst has been investigated in different solvents. The induction period increases in the following order: $CH_3COOEt < Me_2CO < CH_2Cl_2 < THF < CH_3COOH < DMF < DMSO$ [336]. Dimeric Cu(II) μ-hydroxo complexes $[LCu(OH)]_2^{2+}$ catalyze the following selective oxidations with $O_2$: aldehyde to acid (L = bpy); degradation of carbonyl compounds to lower homologues (L = phen); dimerization of phenol (L = phen); alcohol to carbonyl compound (L = phen, in the presence of $Na_2CO_3$) [337]. The autoxidation of PhCHO does not take place in the complete absence of metal cations and is catalyzed by transition metal ions even when these are present only in trace concentrations. All the literature data on the noncatalyzed reaction are regarded as erratic [338].

The oxidation of dihexyl ketone by $O_2$ in the presence of Mn + K stearate catalyst proceeds by initial oxidation of the α-position. The K stearate increases the rate to about twice of that obtained with Mn stearate alone; the initial enolization of the ketone depends on the K stearate [339]. $Mn(st)_2$ and $Mn(OOCCF_3)_2$ did not appreciably alter the rate of free radical formation in the oxidation of 8-pentadecanone. The acceleration of oxidation by $Mn^{2+}$ apparently involved the chain propagation step [340]. Cyclohexanones can be dehydrogenated in the presence of $O_2$ and catalytic amounts of $Pd(OOCCF_3)_2$ at room temperature. No additives are necessary. Phenol was formed at high conversions [341].

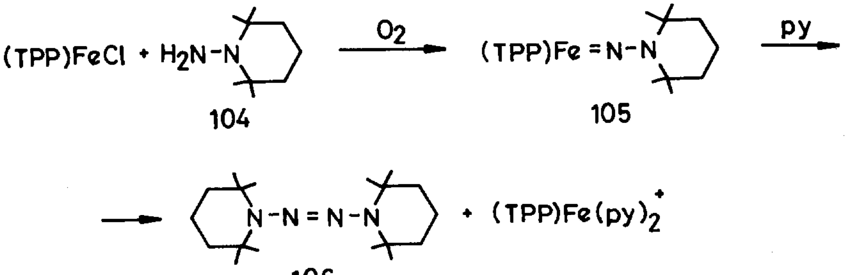
### d) Oxidation of Carboxylic Acids and Derivatives

The oxidation of o-toluic acid was studied using Co(II) and $Br^-$ as catalyst in $Ac_2O$ and HOAc. In $Ac_2O$ phthalic anhydride could be prepared in one step; a large amount of 3-acetoxyphthalide was also formed. In HOAc phthalic acid was the main product, and phthalic anhydride and phthalide were detected as intermediates [342]. A kinetic study indicated that the oxalic acid monoanion was the reactive species in the oxidation of oxalic acid in the presence of Co phthalocyanine [343]. The oxidation kinetics of ascorbic acid by $O_2$ catalyzed by Co(II) tetrasulfophthalocyanine (TSP) was examined in a stopped-flow reactor. Ascorbic acid-$O_2$-Co(II)(TSP) and $O_2$-Co(II)(TSP) are intermediates of the reaction [344]. Addition of glutamic acid significantly reduced the catalytic effect of $Cu^{2+}$ in the oxidation of ascorbic acid, especially in acidic medium [345].

The oxidation of AcOR (R = different alkyls) with a $Co(OAc)_2$ catalyst involves initial oxidation of $Co^{2+}$ to $Co^{3+}$, latter being the active species. HCOOH inhibits the oxidation by reducing $Co^{3+}$ to $Co^{2+}$ [346]. In the oxidation of $Me_2CHCOOMe$ with a $Cu(OAc)_2$ catalyst the copper salt initiates free-radical generation but does not participate in chain propagation or termination [347].

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

The oxidation of Fe(II) oxymesoporphyrin-2-methylimidazole by $O_2$ leads to Fe-mesobiliverdin with the concomitant release of CO from the meso-position of the porphyrin skeleton [348]. The hydrazine (104) reacts with Fe(TPP)Cl in the presence of $O_2$ to form complex (105), from this product the tetrazene (106) is liberated by addition of py [349]:



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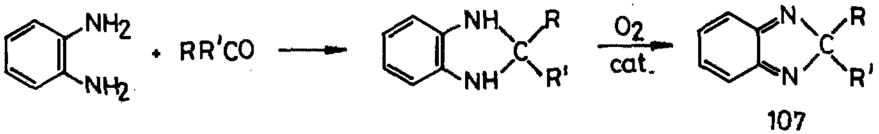
105

106

The complexes $Ru(PPh_3)_2(RNH_2)Cl_2$ (R = $PhCH_2$, $n\text{-}C_5H_{11}$) act as catalysts for the oxidation of the corresponding amines to nitriles by $O_2$. $Ru(PPh_3)_3Cl_2$ reacts with a large excess of benzylamine in the presence of $O_2$ to give $[Ru(PhCH_2NH_2)_5(PhCN)]Cl_2$ which, however, is inactive as an oxidation catalyst [350].

Kinetic data for the $CoBr_2$-catalyzed oxidation of dialkylpyridines by $O_2$ to pyridine-carboxylic acids suggested an inhibiting effect resulting from complexation of Co(II) with the reaction products [351].

The cobaloxime(II) derivatives $Co(Hdmg)_2(PPh_3)_2$ and $[Co(Hdmg)_2py]_2$ catalyzed the oxidation of o-phenylenediamine and ketones by $O_2$ to 2,2-disubstituted 2H-benzimidazoles (107):



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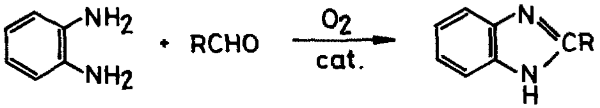
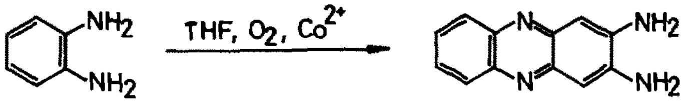
Aldehydes react similarly [352]:



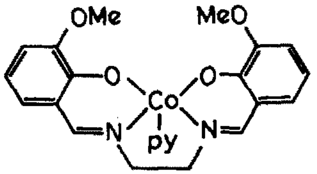
In acetone as solvent with $Co^{2+}$ as catalyst the exclusive product is (107, R = R' = Me). In MeOH and THF (108) is formed with 100% selectivity [353]:



108

The initial rate of adrenochrome formation in the [tetrakis(4-sulfophenyl)porphinato]Co-catalyzed oxidation of adrenaline was directly proportional to the catalyst concentration but was independent of substrate concentration [354]. Co(salen) and its 3,3'-dimethoxy derivative catalyze the oxidation of dihydrazones $H_2NN{=}CRCR'{=}NNH_2$ (R,R' = Ph, p-tolyl, p-anisyl, p-$Me_2NC_6H_4$, p-$ClC_6H_4$) to acetylenes (RC≡CR') under mild conditions [355].

Five-coordinate Co(II)-Schiff base complexes like (109) mediate the oxygenation of p-nitrophenylhydrazones leading to the quantitative formation of 1-(p-nitrophenylazo)-1-peroxy Co(III) complexes of type (110)[356].



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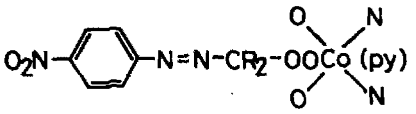

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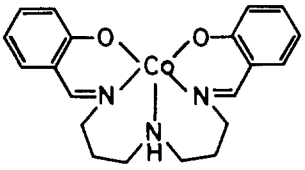
Co(salpr) (111) has been found to promote oxygenation of 2,6-di-tert-butylphenols bearing an electron-withdrawing group in the 4-position. 4-Acyl derivatives (112a) and their oxime O-methyl ethers (112b) gave the corresponding 6-hydroperoxy-2,4-cyclohexadienones (113). The Schiff-bases (114), on the other hand, gave unexpected products (115-7) [357]:



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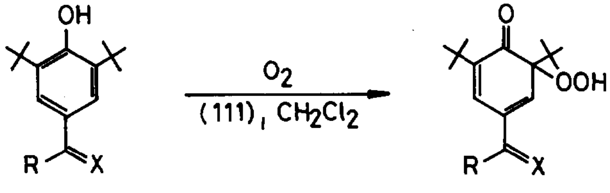


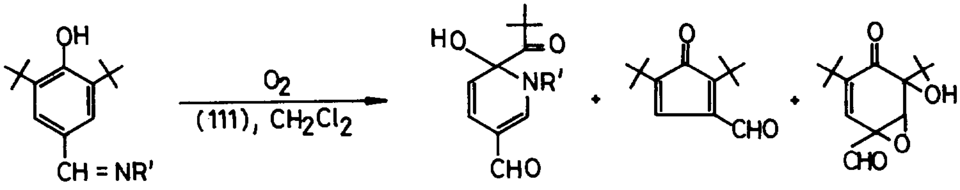
R = H, alkyl, Ph, OMe

R' = alkyl, Cy, $PhCH_2$

112

113

a, X = O ; b, X = NOMe



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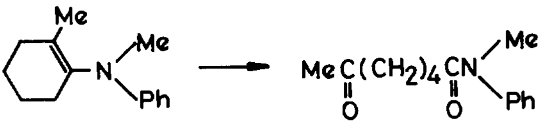
116

117

n-Butyl and n-octyl isocyanide are oxidized by $O_2$ to the corresponding isocyanates and nitrosobenzene to nitrobenzene in the presence of catalytic amounts of cobaloxime(II) complexes [358].

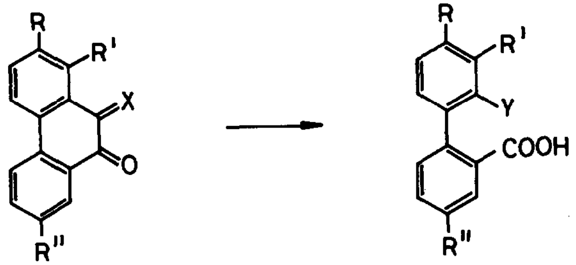
The oxygenation of enamines with $O_2$ and $CuCl_2$ as catalyst leads to double bond cleavage products:



ESR studies show that Cu(II) acts as a one-electron oxidizing agent toward enamines. Kinetic data suggest a mechanism which involves a ternary complex of Cu, enamine and $O_2$ [359]. Diphenylamine was oxidized to tetraphenylhydrazine by $O_2$ in the presence of CuCl in pyridine [360]:

$$2\ Ph_2NH + 1/2\ O_2 \longrightarrow Ph_2N\text{-}NPh_2 + H_2O$$

Depending on the N-substituents, the oxidation of o-phenylenediamines by the system $O_2$ + CuCl + amine yields muconitriles, phenazines, diazo compounds or polymers [361]. 9,10-Phenanthrenequinones (118) and their monoimines (119) are oxygenated by $O_2$ and CuCl in py to give 2,2′-biphenyldicarboxylic acids (120) and 2-cyano-2′-biphenylcarboxylic acids (121)[362]:



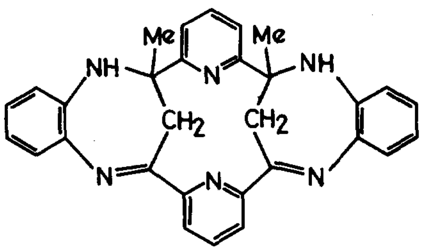
X = O
118

X = NH
119

Y = COOH
120

Y = CN
121

Treatment of (122) with an excess of $Cu(ClO_4)_2.6H_2O$ in refluxing MeOH in the presence of air afforded $[CuL(H_2O)](ClO_4)_2.H_2O$ (L = 123) by oxidative dehydrogenation [363]:



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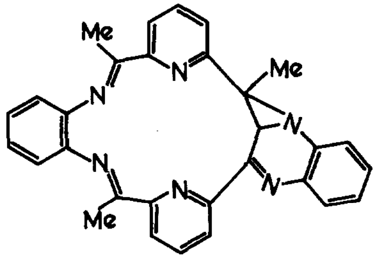
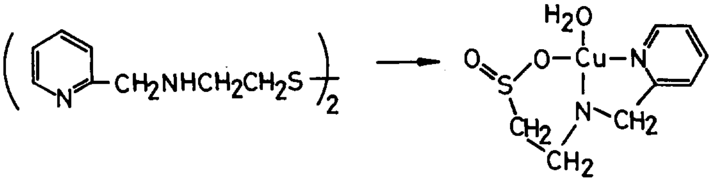


123

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

Air oxidation of $PPh_3$ catalyzed by Mo(VI)-cysteine complexes as $MoO_2(cysOMe)_2$ is enhanced by the addition of hemin or riboflavin. A catalytic cycle is proposed in which these molecules act as electron-transfer mediators for the reoxidation of Mo(V) to Mo(VI) [364]. $Rh_6(CO)_{16}$ catalyzes the oxidation of $PPh_3$, $PMePh_2$, or $AsPh_3$ with $O_2$ to $Ph_3PO$, $MePh_2PO$, or $Ph_3AsO$. In presence of CO, $Rh_6(CO)_{16}$ is reformed. $Rh_4(CO)_8(PPh_3)_4$ and $Rh_2(CO)_6(PPh_3)_2$ are likely intermediates. $Rh_6(CO)_{16}$ and $Re_2(CO)_{10}$ catalyze the autoxidation of ketones and cyclic alcohols to dicarboxylic acids. Experimental data suggest that lower nuclearity Rh carbonyls are active intermediates [365].

The Co(II) chelate of 4,4',4'',4'''-tetrasulphophthalocyanine adsorbed by Sephadex DEAE anion exchange resin is reduced by thiols to the Co(I) form and can be regenerated by air. Accordingly the Co(II)-anion exchange resin system is an efficient catalyst for the autoxidation of thiols [366]. The Na salt of 2-mercaptobenzimidazole is oxidized by $O_2$ to the corresponding disulfide or sulfonic acid in the presence of Co tetrasulphthalocyanine or Co disulfotetraaminophthalocyanine, respectively, as catalyst [367]. Oxidizing disulphide (124) by $O_2$ in the presence of $CuCl_2$ the Cu(II)-sulfinato complex (125) is obtained. The O atoms of the sulfinate moiety originate from $O_2$ and from the water solvent [368]:



124 125

The oxidation of 2-(acetoxymethyl)thiophene with a $Co(OAc)_2$ + NaBr catalyst in AcOH gave ≥ 90% 2-thiophenecarboxylic acid [369]. The toluene derivative (126) was oxidized with a $Co(OAc)_2$ + NaBr catalyst to give (127) in 93-97% yield [370]:

126 127

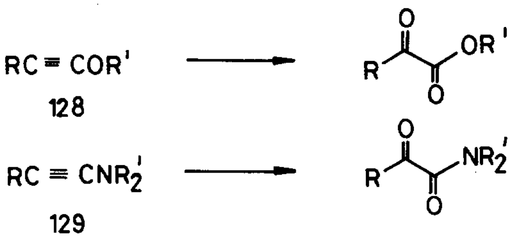
## 5. Catalytic Oxidation of Organic Compounds with Organic or Inorganic Oxidants

### a) Oxidation of Hydrocarbons

Kinetics of the oxidation of octane to a mixture of ketones by tBuOOH + $(Me_3CO)_3VO$ was studied. According to spectral data $(tBuO)_2V(O)OOBu^t$ was the active agent. This complex could be isolated [371]. Ru(IV)chloride complexes catalyze the oxidation of propane and isobutane by strong oxidizing agents such as Cr(VI), $[IrCl_6]^{2-}$, $[SeO_4]^{2-}$, $Cl_2$ and $[S_2O_8]^{2-}$ [372]. The oxidation of propane by $CrO_3$ in aqueous solution of Ru(IV)chloride complexes was investigated. $[Ru(H_2O)(OH)_2Cl_3]^-$ was a more active oxidation catalyst than $[Ru(OH)_2Cl_4]^{2-}$ present at higher $Cl^-$ concentrations [373]. The isolation, purification, characterization and X-ray crystallographic structural analysis of $[Mn(TPP)N_3]_2O$ from the catalytic hydrocarbon hydroxylation system Mn(TPP)X + iodosobenzene ($X = Cl^-$, $Br^-$, $I^-$ and $N_3^-$) has been reported [374].

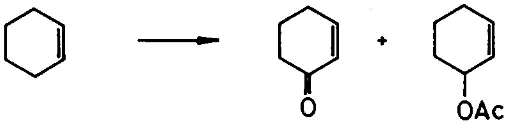
Methods were developed for measuring the rate constants for the reaction of OH radicals with $C_1$-$C_8$ alkanes in $H_2O_2 + Fe^{2+} + Fe^{3+}$ aqueous solutions [375]. A silica-gel adsorbed $Fe^{3+}$-catechol complex prepared from $Fe_2(SO_4)_3$, catechol and silica gel catalyzes the hydroxylation of benzene by $H_2O_2$ [376]. The oxidation of some monocyclic aromatic compounds by $H_2O_2$ in the presence of $Fe(acac)_3$ has been investigated using the aromatic compound also as solvent. The results suggest that - like in aqueous solution - the attacking species is the hydroxyl radical [377]. The products of the reaction of hemes with $O_2$ are peroxy complexes of high-spin Fe(III)-porphyrins. In aprotic solvents these compounds do not oxidize hydrocarbons but can oxidize cyclohexene in presence of $Ac_2O$ [378]. The hydroxylation of cyclohexene and n-heptane with cumylhydroperoxide or iodosobenzene, catalyzed by various metallophorphyrins (Fe, Mn, Co, Rh, Cr) has been compared. The PhIO-dependent hydroxylation is strongly influenced by the nature of the metal and its environment. This is consistent with a metal-oxo-intermediate (porphyrin)M=O. On the contrary, the cumylhydroperoxide-dependent hydroxylation is almost independent of the metal which suggests the cumyloxi radical as the active species [379].

Internal acetylenes $RC\equiv CR'$ [R = R' = Ph; R = Ph, R' = $C_5H_4$, Me; R = Me, R' = Et] are oxidized by iodosobenzene and $Ru(PPh_3)_3Cl_2$ in $CH_2Cl_2$ to give the corresponding $\alpha$-diketones RCOCOR' in good yields. Similarly, terminal acetylenes RC≡CH [R = Ph, $C_6H_{13}$, $C_5H_{11}$] give the corresponding carboxylic acids RCOOH [380]. Oxidation of alkynyl ethers (128) and amines (129) with iodosobenzene in presence of $Ru(PPh_3)_3Cl$ affords α-keto esters and α-keto amides in good yields [381]:



R,R' = alkyl, Ph

Treatment of cyclic olefins with tBuOOH in AcOH and $[Rh_3O(OAc)_6(H_2O)_3]OAc$ as catalyst affords the corresponding α,β-unsaturated carbonyl compounds. Allylic acetates are byproducts [382]:



Application of the same reagent to styrene derivatives resulted in C=C bond fission to give benzaldehyde or acetophenone [382a]:

$$\underset{PhC=CHR}{\overset{H(Me)}{|}} \longrightarrow \underset{PhC=O}{\overset{H(Me)}{|}}$$

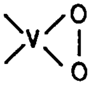
(R = H, Me, Ph, CHO)

The oxidation of cyclic olefins, β-pinene and allylbenzene in acetic acid to the corresponding allylic acetates by tBuOOH is catalyzed by $PdCl_2$, AgOAc and $TeO_2$. Linear α-olefins yield methyl ketones as main products [383]. Relative rate constants were determined for the oxidation of linear alkanes, isoalkanes and cycloalkanes by aqueous $(NH_4)_2S_2O_8$ and $(NH_4)_2S_2O_8 + Ag^+$ systems. The D isotope effect indicated that homolysis of a C-H bond was involved [384].

## b) Epoxidation of Olefins

Perturbation theory was used to examine the decomposition of hydroperoxides and the epoxidation of olefins by hydroperoxides in the presence of metal ions with different electronic structures [385].

Evidence concerning the nature of peroxometal intermediates in the oxidation of organic substrates by $H_2O_2$ or tBuOOH in the presence of vanadium(V) compounds as catalysts indicates that $H_2O_2$ forms a side-bonded peroxometal species (130) whereas tBuOOH forms a V-μ-perester (131)[386]:



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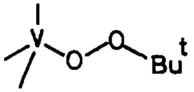


131

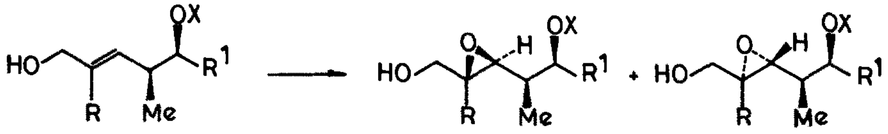
High diastereoselectivities were achieved in the $V^{5+}$-catalyzed tBuOOH epoxidations of acyclic allylic alcohols substituted by the $Me_3Si$ group in the C-2 or C-3 positions [387]. For example:

erythro-epoxide, 100%

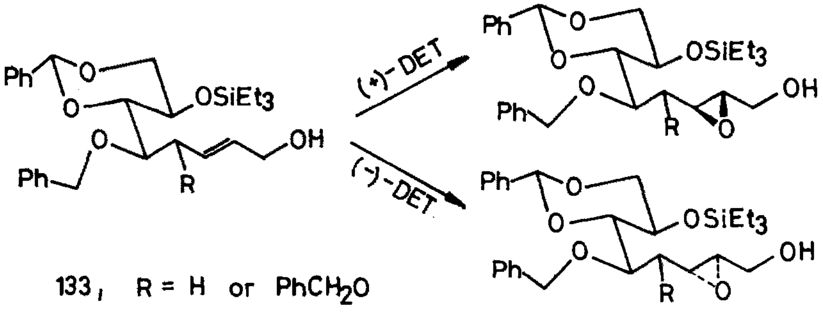
threo-epoxide, 100%

Optimum conditions were established for the epoxidation of α-pinene, geraniol, geraniol acetate, limonene, and methoxycitronellene by tBuOOH in the presence of metal complex catalysts. E.g. oxidation of α-pinene in the presence of $V(acac)_3$ gave 44% of the cis-oxide, whereas in the presence of $Mo(CO)_6$ campholenic aldehyde was obtained [388]. p-Vinylbenzoylacetone was homopolimerized and copolymerized with acrylamide or maleic anhydride to produce polymers which would chelate substantial amounts of transition metal ions such as $Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Eu^{3+}$, and $VO^{2+}$. The $VO^{2+}$ chelate was an effective heterogeneous phase catalyst for the epoxidation of allyl alcohols such as geraniol with tBuOOH [389].

The diastereoselectivity of epoxidation with tBuOOH in presence of $Ti(OPr^i)_4$ has been studied with olefins of type (132) [R = H, Me; $R^1$ = H, $tBuMe_2SiO(CH_2)_4$, $AcOCH_2CH(OMe)C(OMe)_2CH_2$, $PhCH_2CH_2$; X = = $tBuMe_2Si$, $Ph_2MeSi$; $MeO(CH_2)_2OCH_2$, $PhCH_2$] [390]:



The enantioselective Sharpless-epoxidation with tBuOOH, $Ti(OPr^i)_4$ and diethyl tartarate (DET) was used to convert (133) into (134) or (135), depending on the DET enantiomer used [391]:



134

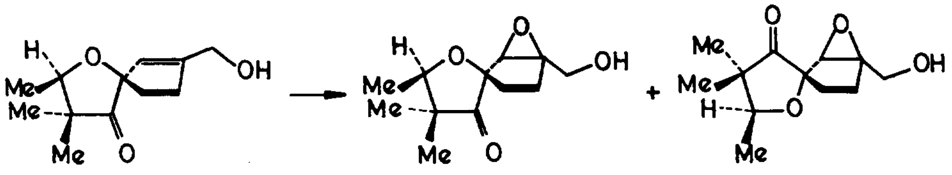
135

133, R = H or $PhCH_2O$

The same system was applied in the presence of (-)-diethyl tartarate for the transformation of (136-8)[392]:

136

Epoxidation of racemic (139) by tBuOOH in the presence of $Ti(OPr^i)_4$ and (-)-diethyl tartarate affords (140) and (141)[393]:

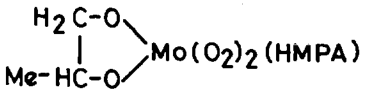


139 140 141

Using the same system [but with (+)-diethyl tartarate] for the epoxidation of (142) afforded (143) in 54% yield [394]:

142 143

Propylene oxide or propane-1,2-diol accelerate the epoxidation of propylene by $MoO(O_2)_2(HMPA)(H_2O)$. Two new epoxidating reagents (144) and (145) are formed and are more active than the parent complex [395]:



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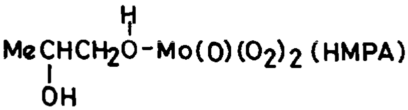
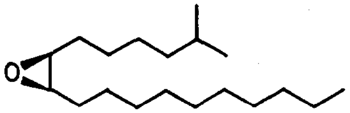


$$\overset{H}{\underset{|}{}}MeCHCH_2\overset{H}{O}{-}Mo(O)(O_2)_2(HMPA)$$
$$\underset{OH}{MeCH}CH_2\overset{H}{O}{-}Mo(O)(O_2)_2(HMPA)$$

145

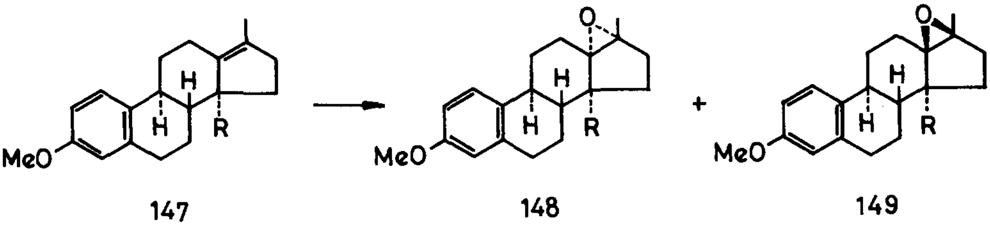
The stoichiometric epoxidation of cyclohexene by $MoO_4L_2$ (L = 8-quinolinol) and $MoO(O_2)_2[OP(NMe_2)_3]$ (A) was nearly 2 orders of magnitude slower than the catalytic epoxidation by tBuOOH in the presence of (A) or $MoO_2L_2$ [396].

$MoO_2L_2$ [HL = $PhCH(OH)CH_2OH$] was prepared and its catalytic activity in epoxidation of propylene by tBuOOH or PhMeCHOOH was studied [397]. Asymmetric epoxidation of (Z)-2-methyl-7-octadecane to disparlure (146) or its enantiomer was carried out in the presence of $MoO_5L$, where L = (-)-$MeOOCCHRCH_2COOMe$ (R = piperidino, morpholino) or (-)-$Et_2NCH_2CHMeCOOMe$ [398]:



146

Based on kinetic experiments a mechanism for the Mo(VI) catalyzed epoxidation of allyl chloride by tBuOOH was proposed [399]. The effects of the initial concentration of 1-nonene, PhMeCHOOH, and Mo complex catalyst on the epoxidation of 1-nonene with ethylbenzene hydroperoxide were determined [400]. $Cp_2MoX_2$ complexes (X = Cl, Br) catalyze the epoxidation of diolefins by tBuOOH in nearly quantitative yield [401]. $MoO_2Cl_2L_2$ ($L_2$ = neutral bidentate or 2 neutral monodentate ligands), $Mo(NO)_2Cl_2L_2$, $Mo(CO)_4L_2$, and polymer-supported Mo complexes catalyze cyclohexene epoxidation. The activity of the catalysts depends on the neutral ligand in the order: $Ph_2P(O)CH_2CH_2P(O)Ph_2$ > bpy > phen. The polymer-supported catalysts were less active than the homogeneous catalysts [402]. Nearly quantitative conversion of (147) into the epoxides (148) and (149) was observed with tBuOOH in presence of $Mo(CO)_6$ in benzene (80°C). The ratio of (148):(149) was 5:1 [403]:



Molybdenum blue adsorbed on charcoal catalyzes the epoxidation of olefins by $H_2O_2$. The addition of alkyltin compounds (e.g. $Me_3SnCl$) increases the yield of epoxide [404].

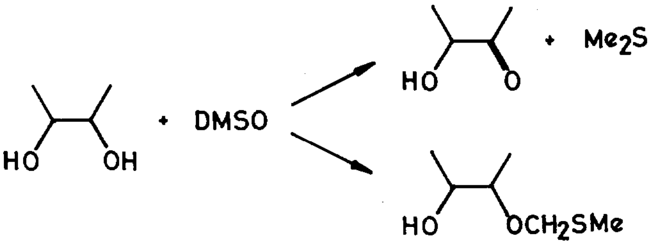
The catalytic activity of Mn(TPP)OAc in the epoxidation of olefins with NaOCl is enhanced by small amounts of pyridine. Pyridine is probably coordinated to the manganese-porphyrin during the reaction [405].

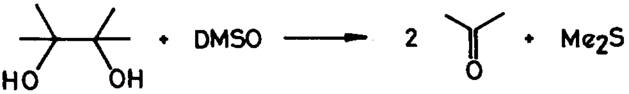
In dry solvents such as THF or $CHCl_3$ oxidation of olefins by $Co(py)(TPP)NO_2$ in the presence of $Tl(OOCPh)_3$ results in moderate yield of epoxides. The source of O is the nitro ligand of the Co complex. Reduction of the Tl(III) cocatalyst is a competing side reaction which deactivates the system [406].

Olefins have been epoxidized with Fe(TPP)Cl and iodosobenzene. The epoxidations are stereospecifically _syn_. The system hydroxylates anisole and naphthalene, but not benzene [407]. Epoxidation of olefins is possible also with p-cyano-N,N-dimethylaniline N-oxide in the presence of Fe(TPP)Cl as catalyst. As a side reaction some oxidative demethylation of the oxidant (yielding formaldehyde) takes place [408].

### c) Oxidation of O-containing Functional Groups

The molybdenum peroxide-catalyzed oxidation of alcohols by DMSO has been applied to 1,2-diols. Monooxidation, dioxidation with C,C-bond cleavage and the formation of 2-methylthiomethoxy-1-ols were observed [409]:





2,2′, 2′′, 2′′′-Tetrapyridineiron(III) complex ions anchored to poly(L-glutamate) or poly(D-glutamate) were used as catalysts for the $H_2O_2$ oxidation of L(+)-ascorbic acid at pH 7 with varying complex:polymer-residue molar ratios. Stereospecific effects were observed on increasing the complex to polymer ratio [410]. The reaction mechanism is complex and comprises a catalytic $[H_2O_2]$-independent pathway and an uncatalyzed electron-transfer process between ascorbate anion and $H_2O_2$ [411].

Ru complexes catalyze the oxidative dehydrogenation of glycerol to glyceraldehyde (and minor amounts of dihydroxiacetone) by N-methylmorpholine oxide. Using $Ru(PPh_3)_2$(aminoacid)Cl complexes a low enantioselectivity was observed [412]. The kinetics of the Ru(III) catalyzed oxidation of aliphatic diols and cyclic alcohols by phenyliodoso acetate in aqueous AcOH + $HClO_4$ is zero order in oxidant and first order in substrate and Ru(III). A mechanism involving $H^-$ abstraction from the alcohol by Ru(III) in the rate-determining step has been proposed [413]. Kinetics of the $RuCl_3$-catalyzed oxidation of several ketones to carboxylic acids by

$NaIO_4$ in aqueous alkaline medium has been reported. The mechanism involves complex formation between $RuCl_3$ species and the ketone [414]. Kinetics for the $RuCl_3$ catalyzed oxidation of triethylene glycol and tetraethylene glycol by $Ce(SO_4)_2$ in aqueous sulfuric acid medium is zero order with respect to $Ce(SO_4)_2$ and first order with respect to substrate and $RuCl_3$. An inner-sphere mechanism involving H-transfer between protonated organic substrate and $RuCl_3$ has been suggested [415].

The Ru(VI)-catalyzed oxidation of 2-Me-propan-1-ol, 3-Me-butan-1-ol, 4-Me-pentan-2-ol, and butan-2-ol by $Fe(CN)_6^{3-}$ was zero order in $Fe(CN)_6^{3-}$ and first order in Ru(VI); the rate increased with substrate concentration and showed Michaelis-Menten behavior. The rate-limiting step is the decomposition of an alcohol-$RuO_4$ complex dianion formed in a steady-state preequilibrium from $HRuO_4^{3-}$ and the corresponding hydroxy carbocation [416]. The kinetics of the $RuCl_3$-catalyzed oxidation of di- and triethylene glycol by $Fe(CN)_6^{3-}$ was studied. A mechanism involving the H-transfer from the $\alpha$-C atom of glycol by the Ru(III) complex was suggested [417]. The oxidation kinetics of $n-C_5H_{11}OH$, $Et_2CHOH$ [418] and benzyl alcohol [419] by $[Fe(CN)_6]^{3-}$ were examined in the presence of Ru complexes.

Trace amounts of $Cu^{2+}$ ions effectively catalyze the oxidation of L-ascorbic acid by $S_2O_8^{2-}$, presumably by the following mechanism [420]:

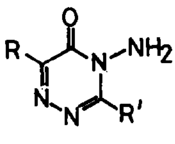
$$[H_2A \rightleftharpoons HA^- + H^+] + Cu^{2+} \longrightarrow Cu^+ + \text{radicals}$$

$$S_2O_8^{2-} + Cu^+ \longrightarrow Cu^{2+} + \cdot SO_4^- + SO_4^{2-}$$

The oxidation of phenylphosphate and hydroquinone phosphate with the $Cu^{2+} + H_2O_2$ system was studied under aerobic and anaerobic conditions [421]. A kinetic study of the Ag(I)-catalyzed oxidation of hexane-1,6-diol by $S_2O_8^{2-}$ was performed [422].

### d) Oxidation of N-containing Compounds

The oxidation of 3,3'-diaminobenzidine (DAB) by $H_2O_2$ catalyzed by $Cu^{2+}$, $Co^{2+}$, $Fe^{3+}$, and $Mn^{2+}$ was investigated. Optimal pH for the reactions in the presence of different metal ions varied from 6 to 9. A rapid spontaneous DAB oxidation by $H_2O_2$ in the absence of any transition metal was observed at pH 5 [423]. The kinetics of the Os(VIII)-catalyzed oxidation of several amino acids by alkaline hexacyanoferrate(III) has been studied. The active oxidizing species is $OsO_4(H_2O)(OH^-)$ [424]. Oxidation of the aminotriazinones (150 a,b) with tBuOOH catalyzed by M(salen) [M = Co(II), Mn(II)] resulted in deamination giving rise to (151 a,b). In the absence of catalyst, (150) is quite stable against tBuOOH. This provides a chemical model for the metabolism of such herbicides [425].



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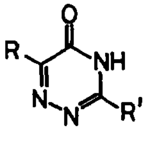


151

a) R = tBu , R' = SMe

b) R = Ph , R' = Me

1,10-Phenanthroline derivatives are oxidized selectively to 2,2'.bipyridine-3,3'-dicarboxylic acids by $H_2O_2$ in the presence of $Co^{2+}$ or $Cu^{2+}$. The mechanism involves reversible attachment of the superoxide ion $O_2^{\bullet -}$ to the C-5:C-6 bond of the starting aromatic compound. The system shows chemiluminescence [426].

### e) Oxidation of S-containing Compounds

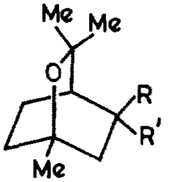
The kinetics of $Ph_2S$ oxidation by $H_2O_2$ in the presence of catalytic amounts of $NaVO_3$ has been determined. The mechanism involves formation of a complex between $H_2O_2$ and $VO_3^-$ and the reaction of this with 2 molecules of $Ph_2S$ [427]. The rates of oxidation of different dialkyl and aryl alkyl sulfides to sulfoxides by $H_2O_2$ or tBuOOH in the presence of catalytic amounts of $VO(acac)_2$ and $MoO_2(acac)_2$ have been measured. Data are best explained by a mechanism according to which the substrate does not coordinate to the metal (external O-transfer mechanism) [428]. The same mechanism applies if $TiO(acac)_2$ is the catalyst, but in this case non-bulky sulfides coordinate to the metal and inhibit their oxidation [429]. The oxidation of aryl methyl sulphides with tBuOOH in the presence of $TiO(acac)_2$ or $Ti(OPr^i)_4$ affords the corresponding sulphoxides in quantitative yield. The kinetic behaviour of the reaction suggests that the sulphides coordinate to Ti(IV) [430].

In the oxidation of aryl methyl sulphides with $H_2O_2$ in the presence of $MoO_2(acac)_2$ in EtOH the substituent effect follows a Hammett relationship and supports an electrophilic mechanism [431]. M(TPP)Cl complexes (M = Fe, Mn) catalyze the oxidation of sulfides to sulfoxides by iodosobenzene [432]. Fe(TPP)Cl catalyzes the oxidation of organic sulfides by $H_2O_2$ to sulfoxides. Imidazole accelerates the reaction extremely but is not absolutely essential. Sulfenium radicals are suggested as intermediates [433].

## 6. Stoichiometric Oxidation with High Valent Transition Metal Complexes

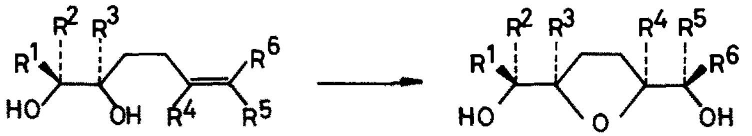
### a) Oxidation of Hydrocarbons

Adamantane, 1-methyladamantane and bicyclo [3.3.1]nonane are oxidized at 25°C by chromic anhydride in 45% $H_2SO_4$ at approximately the same rate, but cyclohexane and methylcyclohexane are oxidized significantly more slowly [434]. Carbon-carbon multiple bonds are oxidatively cleaved by the Cr(V) reagent $(bpy)H_2CrOCl_5$. For example trans-stilbene is converted into benzaldehyde with 96% yield [435]. Oxidation of 1,8-cineole (152, R = R′ = H) with chromyl acetate gave (R, R′ = O) as the major product [436].



152

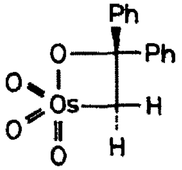
Oxidation of 5,6-dihydroxyalkenes of type (153) derived from neryl and geranyl acetates with Cr(VI) oxo species like Collins reagent ($CrO_3.py_2$) afford cis-THF diols with 99.5% stereospecifity [437]:



153

The homogeneous oxidation of hydrocarbons by $MnO_4^-$ in aqueous solutions is first order in substrate and in Mn(VII). Alkane reactivity increases in the order: $C_2$-$C_6$ n-alkanes < isobutane < cyclohexane < isopentane < methylcyclohexane. The order of C-H bond reactivity is primary < secondary < tertiary [438]. Oxidation of 1-adamantylcarboxylic acid with $KMnO_4$ at 20°C gave mainly the 3-hydroxy derivative. At 80°C the 3-oxo, 3,5-dihydroxy, and 3-hydroxy-5-oxo derivatives were also produced [439]. Oxidation of o-$ROC_6H_4Me$ (R = $PhSO_2$, p-$MeC_6H_4SO_2$, Me) with $KMnO_4$ in aqueous $MgSO_4$ at 90-100°C gave the corresponding benzoic acids o-$ROC_6H_4COOH$ in 75-80% yield [440]. Olefins $RCH{=}CH_2$ (R = $C_{6-20}$ alkyl, Ph) were converted to RCOOH by treatment with $KMnO_4$ in $H_2SO_4$ + AcOH + $CH_2Cl_2$ at room temperature [441]. The oxidation of oleic acid and the cleavage of the carbon-carbon bond was achieved using $KMnO_4$ in water emulsion. The oxidation is controlled by parameters effecting emulsion stability [442]. The oxidation of methyl(E)-cinnamate with quaternary ammonium permanganates is inversely proportional to the size of the cation, i.e. smaller cations promote a faster reaction [443]. [n] Ferrocenophanes are oxidized by $Ba(MnO_4)_2$ to give α-oxo compounds only when n > 3; the yield of oxidation products increases when n = 4,5. In doubly-bridged [n][3]-ferrocenophanes the longer bridge is oxidized more easily [444].

Activation energy and entropy were determined for the oxidation of crotonic acid by alkaline hexacyanoferrate(III) and a mechanism was proposed [445]. The kinetics of oxidation of p-$RC_6H_4COO^-$ (R = Me, Et, iPr) by $Ru(trpy)(bpy)O^{2+}$ to the corresponding α-alcohols in water has been studied. The added O atom comes from the solvent and the oxo group transfer from Ru to the substrate does not occur [446]. $^1H$ NMR investigation of the reaction of $OsO_4$ with 1,1'-diphenylethylene has shown direct evidence for the formation of two asymmetric intermediate species which may be assigned as containing four membered rings with an Os, C bond (154 and 155)[447]:



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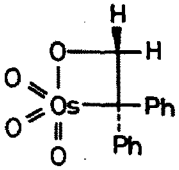
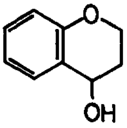


155

Cu(III) oxidizes aromatic and alicyclic compounds in AcOH + $CF_3COOH$, yielding acetates and dehydro dimers [448].

b) Oxidation of O-containing Functional Groups

Rate constants of oxidation of substituted benzyl alcohols with vanadium(V) were determined under pseudo first-order conditions in $HClO_4$-containing solutions. The rate constants and activation parameters did not change significantly with changing the substituents. The main oxidizing species was the V(OH)$_3^{2+}$ cation [449]. The oxidation kinetics of 4-chromanol (156) and 4-chromanone (157) were determined using $V_2O_5$ in $H_2SO_4$.(156) was oxidized first to (157) and then to chromone (158) [450].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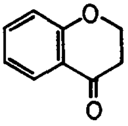
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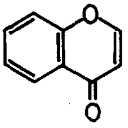
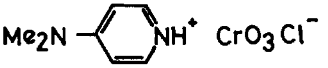

158

The oxidation of alcohols, including carbohydrates by pyridinium chlorochromate (Corey's reagent) or pyridinum dichromate is catalyzed by the addition of molecular sieves. It is postulated that specific sites on the sieves favor hydride-ion transfer [451]. The oxidation of (159) with pyridinum chlorochromate gave (160) or a mixture of (160) + (161) depending on the nature of R [452].

| | | |
|---|---|---|
| $HOCHRCH_2CH=CH_2$ | $RCOCH_2CH=CH_2$ | trans-RCOCH=CHMe |
| (R = H, Ph, Me) | (R = H, Ph, Me) | (R = Me) |
| 159 | 160 | 161 |

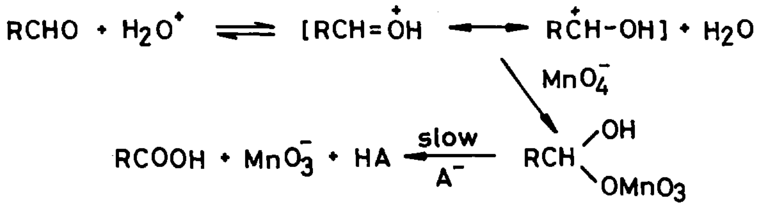
Chromic acid or pyridinium chlorochromate oxidize 9-borabicyclo [3.3.1]nonane to cyclooctanone and cis-1,5-cyclooctanediol to 9-oxabicyclo [3.3.1]nonan-1-ol. Under more drastic conditions pyridinium chlorochromate transforms the latter and cis-1,5-cyclooctanediol to 1,5-cyclooctadiene [453]. 4-Hydroxycyclohexanone was prepared by oxidation of 1,4-cyclohexanediol with poly(4-vinylpyridinium chlorochromate) in $H_2O$ at 80°C with 77% yield [454]. 4-(Dimethylamino)pyridinium chlorochromate (162) is a mild selective reagent for the oxidation of complex allylic and benzylic alcohols to the corresponding carbonyl compounds [455].


162

Pyruvic acid is formed as the major reaction product in the chromic acid oxidation of lactic acid. This points to a two-electron oxidation involving C-H cleavage [456]. Lauryl alcohol is oxidized to n-$C_{11}H_{23}CHO$ in 90% yield by $CrO_3$ on Amberlyst A-26 [457]. Poly[vinyl(pyridinium dichromate)] was prepared from polyvinylpyridine and $CrO_3$ and used to oxidize alcohols to the carbonyl compounds at 70°C. With reactive alcohols ($PhCH_2OH$, PhMeCHOH, $PhCH_2CHCH_2OH$) conversions >99% could be obtained at a 1.1:1 molar ratio of Cr(VI) to alcohol. With aliphatic and alicyclic alcohols a 1.7:1 molar ratio was required. The polymer could be regenerated, treated with $CrO_3$ and reused [458]. Oxidation kinetics of (1-hydroxymethyl)-ferrocene to acetyl-ferrocene with $(Ph_3SiO)_2CrO_2$ were examined in benzene at 20-45°C [459].

$H_4SiMo_{12}O_{40}$ oxidizes a number of O-containing aliphatic compounds. Primary alcohols gave mixtures of ethers and acetals [460]. Colloidal Pt catalyzes the photodehydrogenation of alcohols to aldehydes or ketones by $SiW_{12}O_{20}^{4-}$ [461].

The oxidation of D(+)glucose by $KMnO_4$ in aqueous $H_3PO_4$ solution obeys first order kinetics in both the substrate and the oxidant [462]. The acid-catalyzed reduction of $KMnO_4$ by L-ascorbic acid was studied in $H_2SO_4$. The rate law shows first order dependence in ascorbic acid and fractional dependence in Mn(VII) [463]. The permanganate ion oxidation of 2,2-dimethylpropanal and other aliphatic aldehydes shows general-acid catalysis, is first order in aldehyde and first order in $MnO_4^-$. The following mechanism has been suggested (HA = acid) [464]:



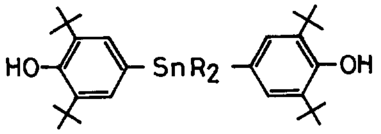
Excellent yields of ketones from secondary alcohols and carboxylic acids from primary alcohols are obtained when the alcohol, dissolved in $CH_2Cl_2$ is added to hydrated copper permanganate and allowed to react for a few minutes [465]. The substituted hydroquinone part of rifamycin B is effectively oxidized to the corresponding quinone structure by $MnO_2$ [466].

Quantitative conversion of alcohols into carbonyl compounds can be effected at 50°C using ferric nitrate impregnated on a K 10 bentonite clay:

$$3\ {>}CHOH + 2\ H^+ + 2\ NO_3^- \longrightarrow 3\ {>}C{=}O + 2\ NO + 4\ H_2O$$

Nitrous esters are intermediates of this reaction [467].

Sterically hindered phenols with Sn, Tl or B-containing groups like (163) and (164) were oxidized by $K_3Fe(CN)_6$ to give 3,3',5,5'-tetra-t-butyl diphenoquinone [468]:



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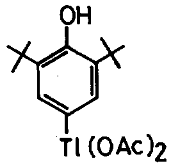


164

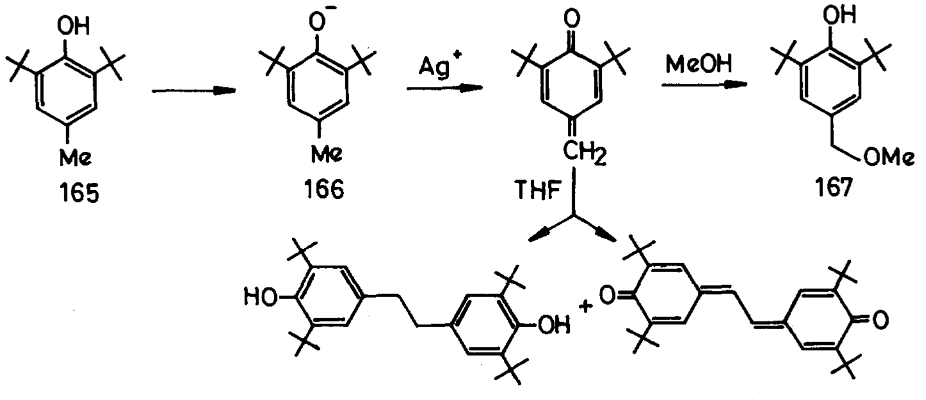
Kinetic and mechanistic studies have been carried out on the oxidation of iPrOH to $Me_2CO$ by $Ru(trpy)(bpy)O^{2+}$, $Ru(bpy)_2(py)O^{2+}$, $Ru(bpy)_2(py)O^{2+}$, $Ru(trpy)(bpy)OH^{2+}$, and $Ru(bpy)_2(py)OH^{2+}$. The results can be interpreted in terms of two-electron oxidation pathways for the Ru(IV) oxo complexes and one-electron pathways for the Ru(III) hydroxy complexes [469].

The oxidative cleavage of 1,2-diols by $Co(OAc)_3$ in AcOH is first order in both Co(III) and substrate [470]. Kinetic studies of the oxidation of L-ascorbic acid by $[Co(C_2O_4)_3]^{3-}$ and $[Fe(phen)]^{3+}$ in aqueous solution support a mechanism of two successive one-electron transfer reactions through an outer-sphere activated complex [471].

Oxidation of $PhCH_2OH$ to acetophenone with $[Ni(bpy)_3]^{3+}$ is first order in both Ni(III) and the alcohol. The second-order rate constant is independent of acidity [472]. Two moles of complex are used for one mole of product. The oxidation is an outer-sphere reaction not requiring the removal of bpy ligands from $Ni^{3+}$ [473]. The kinetics of the oxidation of hydroquinone and catechol by $Ni(III)(1,4,8,11\text{-tetraazacyclotetradecane})^+$ has been studied in detail. Sulfate ions retard the reaction owing to the formation of sulfate complexes with lower redox potentials [474].

The oxidation of L-ascorbic acid and D-isoascorbic acid by the Cu(II) complexes of several polypeptides was investigated. Using enantiomeric polypeptide-Cu(II)complexes stereoselective inhibition was observed, the extent of which depended on pH [475].

The oxidation of $H_2NCH_2CH_2OH$, $HOCH_2CH_2OH$, and several other diols by Ag(II) was studied at pH ≈8,5. Oxidation takes place through intramolecular electron transfer from the substrate to Ag(II) within a complex [476]. Ionol (165) in the form of its conjugated base (166) is oxidized by $Ag^+$ in MeOH to (167) or in THF to (168) and (169) [477]:



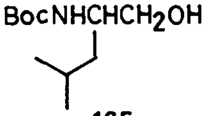
165 166 167

168 169

The potentiomeric study of oxidation of formaldehyde, acetaldehyde, propionaldehyde, and butyraldehyde by ammoniacal silver nitrate indicates that $Ag^+$ and not a $Ag^+$-$NH_3$ complex is the reactive species. The mechanism involves the attack by $Ag^+$ ion on $RCH(OH)_2$ (R = H, Me, Et, Pr) to give Ag, $H^+$, and $^{\cdot}C(OH)_2R$ in the first and rate determining step [478].

### c) Oxidation of N-containing Compounds

Oxidation of the aminoalcohol (165) with $CrO_3$/py in $CH_2Cl_2$ (Collins oxidation) generates the amino aldehyde (166) with complete (>99.5%) retention of chiral integrity [479]:



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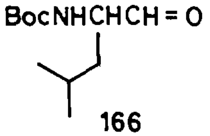
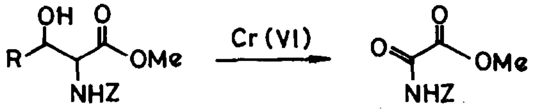


166

Benzyloxycarbonyl threonin (167) and serin (169) methyl esters, when subjected to oxidation with $CrO_3$-pyridine in $CH_2Cl_2$ or $CrO_3$-AcOH, respectively, gave rise to the same N-protected methyl oxamate (169) [480]:

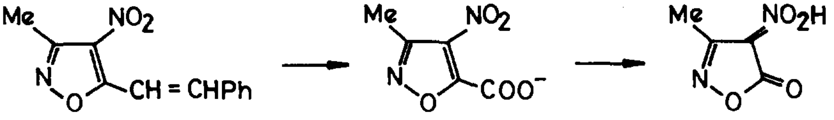
167, R = Me

168, R = H



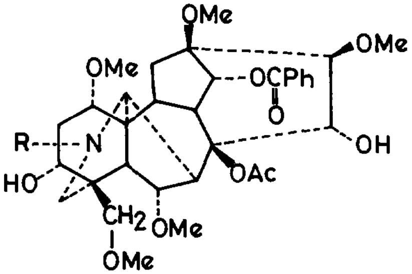
169

Aqueous $KMnO_4$ oxidizes nitro paraffin salts to aldehydes and if the reaction is performed in the presence of a water immiscible solvent like pentane the consecutive oxidation of the aldehyde can be avoided. Yields above 80% can be achieved and even olefinic nitro salts may be converted to unsaturated aldehydes [481]. 1,4-Nitroketones are transformed into 1,4-diketones by treatment with a stoichiometric amount of $KMnO_4$-silica gel in benzene at 70°C in about 70% yield [482]. Permanganate oxidation of (170) gives (172) probably via the unstable carboxylate (171) [483]:



170 171 172

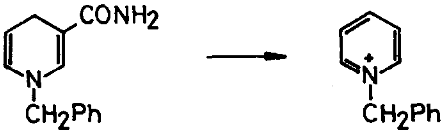
Bispyridinesilver permanganate $Ag(py)_2^+.MnO_4^-$ is a relatively stable compound and soluble in organic solvents like benzene. It is an efficient oxidizing agent for the conversion of alcohols into aldehydes or ketones and aromatic amines into azo compounds [484]. The oxidation of aconitine (173) with $KMnO_4$ has been reinvestigated. The product oxonitine (174) contains an N-formyl group which has been shown now to originate from the solvents acetone and MeOH as well as the acetaldehyde generated by oxidation of the N-ethyl group of aconitine [485].



173, R = Et

174, R = CHO

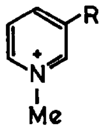
175



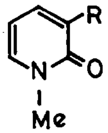
The oxidation of dihydropyridine (175) by $Fe(CN)_6^{3-}$ was studied in weakly basic, neutral, and weakly acidic solutions under an inert atmosphere and in the presence of $O_2$. A mechanism was proposed in which a cation-ferricyanide ion-pair reacts with the substrate to form an ion-radical pair in the rate determining step [486]. The dehydrogenation of hydrazonitriles to azonitriles in an organic solvent by an aqueous solution of $K_3[Fe(CN)_6]$ is catalyzed by carbon black:

$$\text{R-NH-NH-R} \longrightarrow \text{R-N=N-R}$$

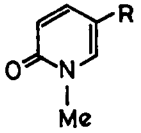
(R = e.g. $Me_2(NC)C-$, $Me(PhCH_2)(NC)C-$). Yields are 99-100%. Phenolic OH groups on the surface of carbon black intermediate this redox reaction [487]. In the oxidation of 3-substituted 1-Me-pyridinium salts (176) with $K_3Fe(CN)_6$, iPr and tBu groups at the 3-position were found to orient oxidation to the 2- and the 6-position. (177) and (178) were formed in ratios of 71:29 and 14:86, respectively [488].



176

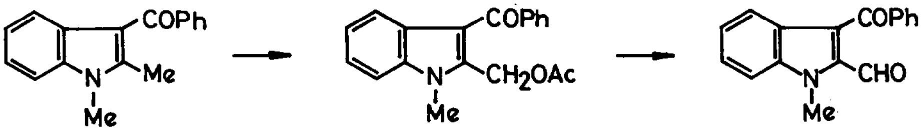


177



178

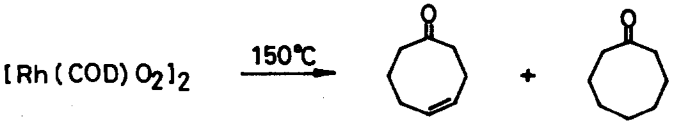
Silver acetate oxidizes (179) in acetic acid solution at reflux temperature to (180) and (181) [489]:



179 180 181

d) Oxidation of P, S, Halogen or Si-containing Compounds

The thermal decomposition of the Rh-$O_2$ complex (182) yields 4-cyclooctenone and cyclooctanone. In the presence of excess $PPh_3$ quantitative formation of $Ph_3PO$ is observed [490]:



182

The oxidation of the 1,2,3,4-thiatriazole-5-thiolate ion by $MnO_4^-$ in alkaline medium was investigated. Two different stoichiometries were observed [491].

The kinetic study of the oxidation of phenol and chlorophenols by alkaline permanganate and by manganate(VI) showed fractional and varying orders with respect to the substrates, thus suggesting free radical chain mechanisms [492]. Oxidation of halotoluenes at 50°C with $Fe(CN)_6^{3-}$ in aqueous AcOH containing $HClO_4$ gave the corresponding aldehyde as the major product. The reaction was first order in substrate, oxidant and acid. A kinetic isotope effect of $k_H/k_D = 6$ was observed. The reaction proceeds via a benzylic radical intermediate [493].

Chromyl chloride reacts regiospecifically with O-silylated enolates to form α-hydroxy ketones. This reaction provides a useful method for the α-hydroxylation of ketones [494].

## V. Reviews

Hydrocarbon reactions on metal centres. 102 refs. [495]

A discussion of the different kinds of solute-solute and solute--solvent interactions acting in homogeneous catalysis by transition metal complexes. 47 refs. [496]

Recent applications of homogeneous catalysis to organic synthesis. 140 refs. [497]

Metal clusters and cluster catalysis. 125 refs. [498]

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Asymmetric synthesis catalyzed by transition-metal complexes with functionalized chiral ferrocenylphosphine ligands. 32 refs. [510]

Chiral ferrocenylphosphines and $\beta$-(N,N-dimethylamino)alkylphosphines: highly efficient ligands for some homogeneous catalytic asymmetric syntheses. 21 refs. [511]

Some asymmetric syntheses catalyzed by chiral phosphine-transition metal complexes. 40 refs. [512]

Asymmetric synthesis mediated by transition metal complexes. 82 refs. [513]

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Stereochemically opened clusters of heavy d-elements in redox catalysis. 52 refs. [515]

Activation and transfer of molecular oxygen catalyzed by transition metal complexes. 153 refs. [516]

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Phase transfer-assisted permanganate oxidations. 97 refs. [519]

Copper catalyzed oxidation and oxygenation 258 refs. [520]

Oxygen-transfer from inorganic and organic peroxides to organic substrates: a common mechanism? 145 refs. [521]

## List of Abbreviations

bpy = 2,2'-bipyridine
COD = 1,5-cyclooctadiene
Cp = $\eta^5$-cyclopentadienyl
Cy = cyclohexyl
CysH = cysteine
diphos = $Ph_2PCH_2CH_2PPh_2$
DMA = dimethyl acetamide

dmgH = dimethylglyoxime
DMSO = dimethyl sulfoxide
dpm = $Ph_2PCH_2PPh_2$
EDTA = ethylene diamine tetraacetic acid
HMPA = hexamethylphosphoric triamide
NBD = norbornadiene
nmen = neomenthyl
o.y. = optical yield
phen = 1,10-phenanthroline
py = pyridine
salen = N,N'-bis salicylidene-ethylenediamino
SIL = silica
st = stearate, $n\text{-}C_{17}H_{35}COO$
TPP = 5,10,15,20-tetraphenylporphinato
trpy = 2,2',2''-terpyridine
ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$
Z = benzyloxycarbonyl, $PhCH_2OCO\text{-}$

## Metal Index

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## References

1 K.M.Nicholas, Organometallics 1 (1982) 1713

2 V.Bellagamba, R.Ercoli and A.Gamba, J.Organometal.Chem. 235 (1982) 201

3 J.P.Daudey, G.Jeung, M.E.Ruiz and O.Novaro, Mol.Phys. 46 (1982) 67; CA 97 (1982) 116059

4 I.V.Repyakh, V.M.Vorontsev and G.I.Golodets, Teor.Eksp.Khim. 18 (1982) 219; CA 97 (1982) 55054

5 A.K.Rappé and W.A.Goddard, J.Am.Chem.Soc. 104 (1982) 3287

6 A.Kiennemann, G.Jenner, E.Bagherzadah and A.Deluzarche, Ind. Eng.Chem., Prod.Res.Dev. 21 (1982) 418

7 L.Kaplan, Organometallics 1 (1982) 1102

8 J.F.Knifton, J.Catal. 76 (1982) 101

9 D.G.Parker, R.Pearce and D.W.Prest, J.C.S.Chem.Commun. (1982) 1193

10 R.J.Daroda and G.Wilkinson, Cienc.Nat. (St.Maria,Braz.) 2 (1980) 33; CA 96 (1982) 51738

11 W.Zhai, Huaxue Tongbao (1981) 582; CA 96 (1982) 103424c

12 T.K.Banerjee, C.R.Saha and D.Sen, J.Chem.Technol. Biotechnol. 31 (1981) 373

13 V.Macho, M.Polievka and E.Jurecekova, Ropa Uhlie 23 (1981) 385; CA 96 (1982) 200312

14 W.Cornely and B.Fell, Chem.Ztg. 105 (1981) 317; CA 96 (1982) 51551

15 T.Fuchikami and I.Ojima, J.Am.Chem.Soc. 104 (1982) 3527

16 V.Macho, E.Jurecekova and M.Polievka, Ropa Uhlie 23 (1981) 329; CA 96 (1982) 51597

17 G.Kohl, M.Kinne, L.Schroeder, H.Fischer, N.S.Imyanitov, B.E.Kuvaev and M.P.Vysotski, Chem.Tech. (Leipzig) 33 (1981) 629

18 W.Cornely and B.Fell, J.Mol.Catal. 16 (1982) 89

19 B.E.Hanson, P.E.Fanwick and J.S.Mancini, Inorg.Chem. 21 (1982) 3811

20 C.U.Pittman, R.H.Ryan, D.W.Wilson, G.Wilemon and M.Absi-Halabi, Prepr.Am.Chem.Soc.Div.Pet.Chem. 25 (1980) 714

21 B.-H.Chang, Inorg.Chim.Acta 65 (1982) L189

22 Yu.B.Kagan, G.A.Korneeva, N.A.Kubasova, M.V.Shishkina, L.I.Zvezdkina and A.N.Bashkirov, Neftekhimiya 21 (1981) 879

23 R.B.King, K.Tanaka, J.Indian Chem.Soc. 59 (1982) 124; CA 97 (1982) 92525

24 C.Claver, E.Marco, L.A.Oro, M.Royo and E.Pastor, Transition Met.Chem. 7 (1982) 246

25 M.Royo, F.Melo, A.Manrique and L.Oro, Transition Met. Chem. 7 (1982) 44

26 S.Arai, T.Saito, H.Matsunaga, M.Sumida, and Y.Tsutsumi Toyo Soda Kenkyu Hokoku 25 (1981) 71; CA 96 (1982) 51741

27 M.Royo, A.Manrique, E.Pastor, L.A.Oro and J.V.Heras, An. Quim.Ser. A 77 (1981) 110; CA 97 (1982) 38277

28 R.Uson, L.A.Oro, M.T.Pinillos, M.Royo and E.Pastor, J.Mol. Catal. 14 (1982) 375

29 M.Matsumoto and M.Tamura, J.Mol.Catal. 16 (1982) 195

30 J.Matsumoto and M.Tamura, J.Mol.Catal. 16 (1982) 209

31 J.D.Unruh and J.R.Christenson, J.Mol.Catal. 14 (1982) 19

32 P.Haelg, G.Consiglio and P.Pino, Helv.Chim.Acta 64 (1981) 1865

33 R.Bardi, A.M.Piazzesi, G.Cavinato, P.Cavoli and L.Toniolo J.Organometal.Chem. 224 (1982) 407

34 R.Bardi, A.M.Piazzesi, A.Del Pra, G.Cavinato and L.Toniolo J.Organometal.Chem. 234 (1982) 107

34a S.C.Tang and L.Kim, J.Mol.Catal. 14 (1982) 231

35 C.U.Pittman, Y.Kawabata, L.I.Flowers, J.C.S.Chem.Commun., (1982) 473

36 G.K.I.Magomedov, and L.V.Morozova, Zh.Obsch.Khim. 51 (1981) 2266

37 T.E.Nalesnik, J.H.Freudenberger and M.Orchin, J.Organometal. Chem. 236 (1982) 95

38 G.Süss-Fink and J.Reiner, J.Mol.Catal. 16 (1982) 231

39 S.I.Woo, and C.G.Hill, J.Mol.Catal. 15 (1982) 309

40 V.A.Semikolenov, B.L.Moroz, V.A.Likholobov and Yu.I. Yermakov, React.Kinet.Catal.Lett. 18 (1981) 341

41 H.Fu, Y.Luo, Z.Yang, Y.Wang, N.Wu and A.Zhang, Youji Hoaxue 6 (1981) 421; CA 96 (1982) 85009

42 B.L.Moroz, V.A.Semikolenov, V.A.Likholobov and Yu.I. Yermakov, J.C.S.Chem.Commun. (1982) 1286

43 L.Vendet and J.K.Stille, Organometallics 1 (1982) 380

44 H.Hirai, Sh.Komatsuzaki and N.Toshima, Nippon Kagaku Kaishi (1982) 316; CA 96 (1982) 199018

45 F.R.Hartley, S.G.Murray and P.N.Nicholson, J.Mol.Catal. 16 (1982) 363

46 A.Luchetti and D.M.Hercules, J.Mol.Catal. 16 (1982) 95

47 F.Jiao, W.Xie, Z.Ma, Y.Yin and Z.Yang, Ranliao Huaxue Xuebao 9 (1981) 47; CA 96 (1982) 52483

48 Z.Tian, Q.Wang and Q.Zhang, Cuihua Xuebao 2 (1981) 83; CA 96 (1982) 103559

49 N.S.Imyanitov, Neftekhimiya 21 (1981) 872

50 T.Okano, T.Kobayashi, H.Konishi and J.Kiji, Tetrahedron Lett. 23 (1982) 4967

51 T.Mise, P.Hong and H.Yamazaki, Chem.Lett. (1982) 401

52 P.Isnard, B.Denise, R.P.A.Sneeden, J.M.Cognion and P.Durual, J.Organometal.Chem. 240 (1982) 169

53 M.J.Chen, H.M.Feder and J.W.Rathke, J.Am.Chem.Soc. 104 (1982) 7346

54 M.J.Chen, H.M.Feder and J.W.Rathke, J.Mol.Catal. 17 (1982) 331

55 M.Röper, H.Loevenich and J.Korff, J.Mol.Catal. 17 (1982) 315

56 J.Gauthier-Lafaye, R.Perron and Y.Colleuille, J.Mol.Catal. 17 (1982) 339

57 K.Kudo and N.Sugita, Nippon Kagaku Kaishi (1982) 462; CA 97 (1982) 55255

58 G.Braca, G.Sbrana, G.Valentini and M.Cini, J.Mol.Catal. 17 (1982) 323

59 M.Hidai, Y.Koyasu, M.Yokota, M.Orisaku and Y.Uchida, Bull. Chem.Soc.Jpn. 55 (1982) 3951

60 J.R.Sweet and W.A.G.Graham, J.Am.Chem.Soc. 104 (1982) 2811

61 T.Bodnar, E.Coman, K.Menard and A.Cutler, Inorg.Chem. 21 (1981) 1275

61a M.A.Drezdzon, K.H.Whitmire, A.A.Bhattacharyya, W.-L.Hsu, C.C.Nagel, S.G.Shore and D.F.Shriver, J.Am.Chem.Soc. 104 (1982) 5630

61b J.N.Nicholls, D.H.Farrar, P.F.Jackson, B.F.G.Johnson and J.Lewis, J.C.S.Dalton Trans. (1982) 1395

62 B.T.Heaton, L.Strona, J.Jonas, T.Eguchi and G.A.Hoffman J.C.S.Dalton Trans. (1982) 1159

63 J.H.Freudenberger and M.Orchin, Organometallics 1 (1982) 1408

64 M.J.Nappa, R.Santi, S.P.Diefenbach, and J.Halpern, J.Am. Chem.Soc. 104 (1982) 619

65 J.C.Barborak and K.Cann, Organometallics 1 (1982) 1726

66 F.Ungváry and L.Markó, Organometallics 1 (1982) 1120

67 R.U.Kastrup , J.S.Merola and A.A.Oswald, Adv.Chem.Ser. 196 (1982) 43

68 J.M.Brown, L.R.Canning, A.G.Kent and P.J.Sidebottom, J.C.S. Chem.Commun. (1982) 721

69 J.M.Brown and A.G.Kent, J.C.S.Chem.Commun. (1982) 723

70 A.A.Oswald, J.S.Merola, E.J.Mozeleski, R.V.Kastrup and J.C. Reisch, ACS Symp.Ser. 171 (Phosphorus Chem.) (1981) 503

71 D.J.Darensbourg and A.Rokicki, Organometallics 1 (1982) 1685

72 W.A.R.Slegeir, R.S.Sapienza, R.Rayford and L.Lam, Organometallics 1 (1982) 1728

73 S.Attali, R.Mathieu and G.J.Leigh, J.Mol.Catal. 14 (1982) 293

74 R.G.Pearson and H.Mauermann, J.Am.Chem.Soc. 104 (1982) 500

75 D.C.Gross and P.C.Ford, Inorg.Chem. 21 (1982) 1702

76 J.C.Bricker, C.C.Nagel and S.G.Shore, J.Am.Chem.Soc. 104 (1982) 1444

77 D.Choudhury and D.J.Cole-Hamilton, J.C.S.Dalton Trans. (1982) 1885

78 S.Bhaduri, H.Khwaja and K.R.Sharma, Indian J.Chem. 21A (1982) 155

79 D.Forster and T.C.Singleton, J.Mol.Catal. 17 (1982) 299

80 C.P.Kubiak, C.Woodcock and R.Eisenberg, Inorg.Chem. 21 (1982) 2119

81 A.A.Frew, R.H.Hill, L.Manojlovic-Muir, K.W.Muir and R.J. Puddephat, J.C.S.Chem.Commun. (1982) 198

82 T.Okano, T.Kobayashi, H.Konishi and J.Kiji, Bull.Chem.Soc.Jpn. 55 (1982) 2675

83 K.Kaneda, M.Yasumura, T.Imanaka and S.Teranishi, J.C.S.Chem. Commun. (1982) 935

84 T.J.Lynch, M.Banah, M.McDougall and H.D.Kaesz, J.Mol.Catal. 17 (1982) 109

85 R.H.Fish, A.D.Thormodsen and G.A.Gremer, J.Am.Chem.Soc. 104 (1982) 5234

86 Y.Watanabe, N.Suzuki, Y.Tsuji, S.C.Shim and T.Mitsudo, Bull. Chem.Soc.Jpn. 55 (1982) 1116

87 T.Okano, K.Fujiwara, H.Konishi and J.Kiji, Bull.Chem.Soc.Jpn. 55 (1982) 1975

88 J.Palágyi and L.Markó, J.Organometal.Chem. 236 (1982) 343

89 K.Murata and A.Matsuda, Bull.Chem.Soc.Jpn. 55 (1982) 2195

90 F.Jachimowicz and J.W.Raksis, J.Org.Chem. 47 (1982) 445

91 J.K.Hoyano and W.A.G.Graham, J.Am.Chem.Soc. 104 (1982) 3723

92 E.S.Rudakov, V.P.Tret'yakov, S.A.Mitchenko and A.V.Bogdanov Dokl.Akad.Nauk SSSR 259 (1981) 899

93 A.F.Shestakov, S.Ya.Zhuk, A.T.Papoyan and E.A.Grigoryan Kinet.Katal 23 (1982) 597

94 W.J.S.Lockley, Tetrahedron Lett. 23 (1982) 3819

95 R.L.Whetten, K.J.Fu and E.R.Grant, J.Chem.Phys. 77 (1982) 3769

96 L.N.Sukhobok, G.P.Potapov, V.G.Luksha, V.N.Krutii and B.D.Polkovnikov, Izv.Akad.Nauk SSSR, Ser.Khim. (1982) 2310

97 Y.Doi, K.Koshizuka and T.Keii, Inorg.Chem. 21 (1982) 2732

98 Y.Doi, S.Tamura and K.Koshizuka, Inorg.Chim.Acta 65 (1982) L63

99 K.J.McQuade, R.Pierantozzi, M.B.Freeman and B.C.Gates Prepr.Am.Chem.Soc.,Div.Pet.Chem. 25 (1980) 751

100 B.Besson, A.Choplin, L.D'Ornelas and J.M.Basset, J.C.S.Chem. Commun. (1982) 843

101 F.K.Shmidt, Yu.S.Levkovskii, N.M.Ryutwa, and T.I.Bakunina Kinet.Katal. 23 (1982) 360

102 G.V.Tsintsadze, E.D.Getsadze, E.F.Litvin, and L.Kh.Freidlin Soobshch .Akad.Nauk Gruz.SSR 104 (1981) 57; CA 96 (1982) 180693

103 G.Vitulli, P.Salvadori, A.Raffaelli, P.A.Costantino and R.Lazzaroni, J.Organometal.Chem. 239 (1982) C23

104 J.E.Hamlin, K.Hirai, V.C.Gison and P.M.Maitlis, J.Mol.Catal. 15 (1982) 337

105 M.Carvalho, L.F.Wieserman and D.M.Hercules, Appl.Spectrosc. 36 (1982) 290

106 J.R.Peterson, D.W.Bennett and L.D.Spicer, J.Catal. 71 (1981) 223

107 H.H.Seltzman, S.D.Wyrick and C.G.Pitt, J.Labelled Compd. Radiopharm. 18 (1981) 1365

108 S.Cenini, R.Ugo and F.Porta, Gazz.Chim.Ital. 111 (1981) 293

109 G.M.Grishina, A.T.Teleshev, E.E.Nifant'ev, Zh.Obsch.Khim. 52 (1982) 1307

110 R.T.Smith, R.K.Ungar and M.C.Baird, Transition Met.Chem. 7 (1982) 288

110a J.Niewahner and D.W.Meek, Inorg.Chim.Acta 64 (1982) L123

111 J.Niewahner and D.W.Meek, Adv.Chem.Ser. 196 (1982) 237

112 A.Efraty and I.Feinstein, Inorg.Chem. 21 (1982) 3115

113 T.Uematsu and H.Hashimoto, Kogakubu Kenkyu Hokoku (Chiba Daigaku) 33 (1981) 99; CA 96 (1982) 110835

114 I.V.Patsevich, I.A.Ogorodnikov, A.I.Fridman, V.I.Nefedov, and Ya.V.Salyn, Vysokomol.Soedin.,Ser.A 24 (1982) 1559; CA 97 (1982) 127352

115 Z.Chen, Y.Jiang, Fundam.Res.Organomet.Chem.Proc.China-Jpn-U.S.Trilateral Semin.Organomet.Chem.,1st (1980) 629; CA 97 (1982) 128222

116 M.Capka, Kinet.Katal. 23 (1982) 291

117 R.H.Crabtree, P.C.Demou, D.Eden, J.M.Mihelcic, C.A.Parnell, J.M.Quirk and G.E.Morris, J.Am.Chem.Soc. 104 (1982) 6994

118 Ch.J.Moon, Ch.Sh.Chin, Taehan Hwahakhoe Chi 26 (1982) 253 ; CA 97 (1982) 215504

119 R.Uson, L.A.Oro, M.J.Fernandez and R.Sariego, Rev.Acad. Cienc.Exactas, Fis.-Quim.Nat.Zaragoza 35 (1980) 87; CA 97 (1982) 215423

120 F.Morandini, B.Longato and S.Bresadola, J.Organometal.Chem. 239 (1982) 377

121 A.S.Berenblyum, A. Knizhnik, S.L.Mund and I.I.Moiseev, J.Organometal.Chem. 234 (1982) 219

122 A.S.Berenblyum, A.Knizhnik, S.L.Mund, and I.I.Moiseev, Izv. Akad.Nauk SSSR, Ser.Khim. (1982) 1249

123 A.S.Berenblyum, S.L.Mund, T.P.Goranskaya and I.I.Moiseev Izv.Akad.Nauk SSSR, Ser.Khim. (1981) 2472

124 Y.Chen, J.Liu, Y.Lin, J.Ni, Ch.Xiao, and Y.Wan, Wuhan Daxue Xuebao, Ziran Kexueban (1982) 41; CA 97 (1982) 61687

125 Y.Lin, J.Liu, J.Ni, Y.Chen, Ch.Xiao and Y.Wang, Cuihua Xuebao 3 (1982) 220; CA 97 (1982) 215076

126 D.Wang, Y.Zhou, Y.Jiang, Ch.Chen, Sh.Li and B.Kang, Gaofenzi Tongxun (1982) 78; CA 97 (1982) 163746

127 B.Chen, Zh.Peng and R.Chen, Fundam.Res.Organomet.Chem., Proc.China-Jpn-U.S.Trilateral Semin.Organomet.Chem. 1st (1980) 613; CA 97 (1982) 72918

128 V.N.Kolot, M.V.Lyubimilova, E.F.Litvin, G.I.Kudryavtsev, L.Kh.Freidlin and S.L.Davidova, Izv.Akad.Nauk SSSR, Ser. Khim. (1982) 1420

129 T.P.Voskresenkaya, V.A.Semikolenov, V.A.Likholobov, A.P.Shepelin, P.A.Zhdan and A.V.Mashkina, Kinet.Katal. 23 (1982) 382

130 V.A.Semikolenov, V.A.Likholobov, and Yu.I.Ermakov, Kinet. Katal. 22 (1981) 1475

131 Y.Zhou, and Y.Jiang, Guihua Xuebao 2 (1981) 233; CA 96 (1982) 4154

132 K.Kushi, Y.Matsumura, K.Hiroyoshi, K.Tarama and S.Yoshida Nippon Kagaku Kaishi (1982) N$^{o}$ 3, 347; CA 97 (1982) 5579

133 J.L.Graff, T.J.Sobieralski, M.S.Wrighton and G.L.Geoffroy J.Am.Chem.Soc. 104 (1982) 7526

134 L.J.Boucher, N.J.Holy and B.H.Davis, ACS Symp.Ser. 169 (1981) 319

135 S.Koritala, JAOCS, J.Am.Oil Chem.Soc. 59 (1982) 309

136 J.M.Brown and D.Parker, J.Org.Chem. 47 (1982) 2722

137 J.M.Brown and P.A.Chaloner, J.C.S.Perkin Trans. II (1982) 711

138 D.P.Riley, J.Organometal.Chem. 234 (1982) 85

139 C.Cativiela, J.Fernandez, J.A.Mayoral, E.Melendez, R.Uson, L.A.Oro and M.J.Fernandez, J.Mol.Catal. 16 (1982) 19

140 P.Salvadori, R.Lazzaroni, A.Raffaelli, S.Pucci , S.Bertozzi, D.Pini and G.Fatti, Chim.Ind. (Milan) 63 (1981) 492

141 W.R.Cullen and J.D.Woollins, Can.J.Chem. 60 (1982) 1793

142 T.Yoshikuni and J.C.Bailar, Inorg.Chem. 21 (1982) 2129

143 J.M.Brown, and B.A.Murrer, J.C.S.Perkin Trans.II (1982) 489

144 J.P.Amma, and J.K.Stille, J.Org.Chem. 47 (1982) 468

145 D.Lafont, D.Sinou and G.Descotes, J.Chem.Res.,Synop. (1982) 117

145a H.Brunner and M.Pröbster, Inorg.Chim.Acta 61 (1982) 129

146 W.S.Knowles, W.C.Christopfel, K.E.Koenig, and C.F.Hobbs Adv.Chem.Ser. 196 (1982) 325

147 A.Miyashita, H.Takaya and R.Noyori, ACS Symp.Ser. 185 (1982) 274

148 K.Toriumi, T.Ito, H.Takaya, T.Souchi and R.Noyori, Acta Christallogr. B38 (1982) 807

149 A.Uehara and J.C.Bailar, J.Organometal.Chem. 239 (1982) 1

150 G.Comisso, A.Sega, V.Sunjic and A.Lisini, Croat.Chem.Acta 54 (1981) 375; CA 97 (1982) 92397

151 M.Yamashita, K.Hiramatsu, M.Yamada, N.Suzuki and S.Inokawa Bull.Chem.Soc.Jpn. 55 (1982) 2917

152 J.Bourson and L.Oliveros, J.Organometal.Chem. 229 (1982) 77

153 E.Casarotti, A.Chiesa and G.D'Alfonso, Tetrahedron Lett. 23 (1982) 2995

154 E.E.Nifantev and T.S.Kukhareva, Zh.Obshch.Khim. 51 (1981) 2146

155 I.Ojima, T.Kogure, N.Yoda, T.Suzuki, M.Yatabe and T.Tanaka J.Org.Chem. 47 (1982) 1329

156 I.Ojima and M.Yatabe, Chem.Lett. (1982) 1335

157 I.Ojima and N.Yoda, Tetrahedron Lett. 23 (1982) 3913

158 I.Ojima, N.Yoda and M.Yatabe, Tetrahedron Lett. 23 (1982) 3917

159 J.-C.Poulin and H.B.Kagan, J.C.S.Chem.Commun. (1982) 1261

160 V.K.Latov, A.I.Vinogradova, M.B.Saporovskaja and V.M.Belikov Izv.Akad.Nauk SSSR, Ser.Khim (1982) 683

161 J.M.Brown and R.G.Naik, J.C.S.Chem.Commun. (1982) 348

162 J.M.Brown and D.Parker, Organometallics 1 (1982) 950

163 T.-P.Dang, P.Aviron-Violet, Y.Colleuille and J.Varagnat J.Mol.Catal. 16 (1982) 5

164 L.O.Nindakova, F.K.Shmidt, E.L.Klabunovskii, V.N.Sheveleva and U.A.Pavlov, Izv.Akad.Nauk.SSSR, Ser.Khim (1981) 2621

165 A.Uehara and J.C.Bailar, J.Organometal.Chem. 239 (1982) 11

166 H.Kanai, N.Yamamoto, K.Kishi, K.Mizuno and K.Tarama, J.Catal. 73 (1982) 228

167 P.M.Lausarot, G.A.Vaglio and N.Valle, J.Organometal.Chem. 240 (1982) 441

168 R.R.Burch, E.L.Muetterties, R.G.Teller and J.M.Williams, J.Am.Chem.Soc. 104 (1982) 4257

169 A.R.Sanger, Can.J.Chem. 60 (1982) 1363

170 D.J.A. de Wall, T.I.A.Gerber and W.J.Louw, J.C.S.Chem. Commun. (1982) 100

171 M.Sakai, F.Harada, Y.Sakakibara and N.Uchino, Bull.Chem.Soc. Jpn. 55 (1982) 343

172 G.V.Kudryavtsev, A.Yu.Stekheev and G.U.Lisichkin, Zh.Vses. Khim. O-va. 27 (1982) 232; CA 97 (1982) 38120

173 S.Franks, F.R.Hartley and J.R.Chipperfield, Adv.Chem.Ser.196 (1982) 273

174 A.Fusi, R.Ugo, R.Psaro, P.Braunstein and J.Dehand, J.Mol. Catal. 16 (1982) 217

175 P.Le Maux and G.Simonneaux, J.Organometal.Chem. 229 (1982) C24

176 M.J.Mirbach, T.N.Phu and A.Saus, J.Organometal.Chem. 236 (1982) 309

177 Ch.Zhao, Y.Zhou, L.Wang and Sh.Chin, Lanzhou Daxue Xuebao, Ziran Kexueban 18 (1982) 121; CA 97 (1982) 164906

178 Z.Dawoodi, K.Henrick and M.J.Mays, J.C.S.Chem.Commun. (1982) 696

179 M.Pasquali, P.Leoni, C.Floriani, and A.Gaetani-Manfredotti, Inorg.Chem. 21 (1982) 4324

180 W.J.Evans, D.J.Wink and D.R.Stanley, Inorg.Chem. 21 (1982) 2565

181 V.E.Zadov, A.V.Finkelshtein and A.A.Vaisburd, Dokl.Akad. Nauk SSSR 263 (1982) 922

182 V.E.Zadov, A.V.Finkelshtein and A.A.Vaisburd, Kinet.Katal. 23 (1982) 838

183 V.E.Zadov, A.V.Finkelshtein, A.A.Vaisburd and O.U.Yangalov Kinet.Katal. 23 (1982) 630

184 I.Rajca, Pol.J.Chem. 55 (1981) 775; CA 97 (1982) 91423

185 T.Okano, K.Tsukiyama, H.Konishi and J.Kiji, Chem.Lett. (1982) 603

186 M.Yamashita, K.Miyoshi, Y.Okada and R.Suemitsu, Bull.Chem. Soc.Jpn. 55 (1982) 1329

187 G.Lavigne, N.Lugan and J-J.Bonnet, Organometallics 1 (1982) 1040

188 B.R.Cho and R.M.Laine, J.Mol.Catal. 15 (1982) 383

189 K.Tani, K.Suwa, E.Tanigawa, T.Yoshida, T.Okano and S.Otsuka, Chem.Lett. (1982) 261

190 S.Badhuri, K.R.Sharma, J.C.S.Dalton Trans. (1982) 727

191 S.Tőrös, L.Kollár, B.Heil and L.Markó, J.Organometal.Chem. 232 (1982) C17

192 F.Joó and E.Trócsányi, J.Organometal.Chem. 231 (1982) 63

193 K.Tani, K.Suwa, T.Yamagata and S.Otsuka, Chm.Lett. (1982) 265

194 K.Tani, K.Suwa and S.Otsuka, ACS Symp.Ser. 185 (1982) 283

195 M.Kumada, T.Hayashi, T.Mise, A.Katsumara, N.Nagashima and M.Fukushima, Kenkyu Hokoku-Asahi Garasu Kogyo Gijutsu Shoreikai 37 (1980) 69; CA 96 (1982) 85708

196 J.Bremer, V.Dexheimer and K.Madeja, J.Prakt.Chem. 323 (1981) 857

197 A.Rockenbauer, M.Györ, M.Kwiecinski and S.Tyrlik, Inorg. Chim.Acta 58 (1982) 237

198 T.K.Banerjee and D.Sen, J.Chem.Technol.Biotechnol. 31 (1981) 676

199 M.V.Klyuev, Uzv.Vyssh.Uchebn.Zaved.,Khim.Khim.Tekhnol. 25 (1982) 751; CA 77 (1982) 99077

200 D.J.Drury, M.J.Green, D.J.M.Ray and A.J.Stevenson, J.Organometal.Chem. 236 (1982) C23

201 H.Fujitsu, E.Matsumara, S.Shirahama, K.Takeshita and I.Mochida, J.C.S.Perkin Trans.I (1982) 855

202 J.Banford, Z.Dawoodi, K.Henrick and M.M.Mays, J.C.S.Chem. Commun. (1982) 554

203 C.W.Jung and P.E.Garrov, Organometallics 1 (1982) 658

204 S.Shinoda, Y.Tokushige, T.Kojima and Y.Saito, J.Mol.Catal. 17 (1982) 81

205 H.Moriyama, T.Aoki, S.Shinoda and Y.Saito, J.C.S.Perkin Trans. II (1982) 369

206 L.F.Halle, R.Houriet, M.M.Kappes, R.H.Staley and J.L. Beauchamp, J.Am.Chem.Soc. 104 (1982) 6293

207 R.S.Paonessa and W.C.Trogler, J.Am.Chem.Soc. 104 (1982) 3529

208 H.Inoue and M.Sato, J.C.S.Chem.Commun. (1982) 1014

209 D.Baudry, M.Ephritikhine and H.Felkin, J.C.S.Chem.Commun. (1982) 606

210 D.Baudry, M.Ephritikhine, H.Felkin and J.Zakrewski, J.C.S. Chem.Commun. (1982) 1235

211 R.H.Crabtree, M.F.Mellea, J.M.Mihelcic and J.M.Quirk, J.Am. Chem.Soc. 104 (1982) 107

211a R.R.Burch, E.L.Muetterties and V.W.Day, Organometallics, 1 (1982) 188

212 A.Vazquez de Miguel, K.Isobe, B.F.Taylor, A.Nutton and P.M.Maitlis, J.C.S.Chem.Commun. (1982) 758

213 R.Usón, L.A.Oro and M.A.Esteruelas, Transiion Met.Chem. 7 (1982) 242

214 D.Beaupere, L.Nadjo, R.Uzan and P.Bauer, J.Mol.Catal. 14 (1982) 129

215 D.Beaupere, P.Bauer, L.Nadjo and R.Uzan, J.Organometal. Chem. 238 (1982) C12

216 J.Kaspar, R.Spigliarich and M.Graziani, J.Organometal.Chem. 231 (1982) 71

217 R.Spogliarich, A.Tencich, J.Kaspar and M.Graziani, J.Organometal.Chem. 240 (1982) 453

218 S.Muthukamaru Pillai, S.Vancheesan, J.Rajaram and J.C. Kuriacose, J.Mol.Catal. 16 (1982) 349

219 R.Sariego and L.A.Oro, Bol.Soc.Chil.Quim. 27 (1982) 62; CA 97 (1982) 45017

220 R.Sariego, M.Valderrama, I.Carkovic, M.Martinez, Bol.Soc. Chil.Quim. 27 (1982) 117; CA 97 (1982) 55045

221 Y.Watanabe, T.Ohta and Y.Tsuji, Bull.Chem.Soc.Jpn. 55 (1982) 2441

222 R.Grigg, T.R.B.Mitchell and S.Sutthivaiyakit, Tetrahedron 37 (1981) 4313

223 M.Bianchi, U.Matteoli, P.Frediani, G.Menchi and F.Piacenti J.Organometal.Chem. 240 (1982) 59

224 M.Bianchi, U.Matteoli, P.Frediani, G.Menchi and F.Piacenti J.Organometal.Chem. 236 (1982) 375

225 R.Spogliarich. G.Zassinovich, J.Kaspar and M.Graziani, J.Mol. Catal. 16 (1982) 359

226 Y.Ishii, K.Osakada, T.Ikariya, M.Saburi and S.Yoshikawa Chem.Lett. (1982) 1179

227 M.Bianchi, U.Matteoli, G.Menchi, P.Frediani and F.Piacenti J.Organometal.Chem. 240 (1982) 65

228 K.F.Liou and C.H.Cheng, J.Org.Chem. 47 (1982) 3018

229 W.J.Boyle and F.Mares, Organometallics 1 (1982) 1003

230 Y.Nambu, M.Kijima, T.Endo and M.Okawara, J.Org.Chem. 47 (1982) 3066

231 J.Blum, S.Shtelzer, P.Albin and Y.Sasson, J.Mol.Catal. 16 (1982) 167

232 R.Bar, Y.Sasson and J.Blum, J.Mol.Catal. 16 (1982) 175

233 Ch.Qian, K.Liu and H.Zhou, Huaxue Xuebao 40 (1982) 165; CA 96 (1982) 199011

234 M.R.Churchill, H.J.Wasserman, P.A.Belmonte and R.R.Schrock Organometallics 1 (1982) 559

235 J.B.N.Effa, J.Lieto and J.P.Aune, Inorg.Chim.Acta 65 (1982) L105

236 T.E.Nalesnik and M.Orchin, Organometallics 1 (1982) 222

237 J.A.Roth, P.Wiseman and L.Ruszala, J.Organometal.Chem. 240 (1982) 271

238 T.E.Nalesnik, J.H.Freudenberger and M.Orchin, J.Mol.Catal. 16 (1982) 43

239 Y.Matsui and M.Orchin, J.Organometal.Chem. 236 (1982) 381

240 O.V.Howarth, C.H.McAteer, P.Moore and G.E.Morris, J.C.S. Chem.Commun. (1982) 745

241 R.Amposta, P.Camps, M.Figuredo, C.Jaime and A.Virgili An.Quim.Ser. C 77 (1981) 267; CA 97 (1982) 162429

242 D.R.Corbin, G.D.Stucky, W.S.Willis and E.G.Sherry, J.Am. Chem.Soc. 104 (1982) 4298

243 T.Y.Luh, Synth.Commun. 11 (1981) 829

244 J.-J.Brunet, D.Besozzi, A.Courtois and P.Caubere, J.Am.Chem. Soc. 104 (1982) 7130

245 G.Folcher, J.F.Le Maréchal and H.Marquet-Ellis, J.C.S.Chem. Commun. (1982) 323

246 Y.D.Xing and N.Z.Huang, J.Org.Chem. 47 (1982) 140

247 N.Ueyama, M.Nakata and A.Nakamura, J.Mol.Catal. 14 (1982) 341

248 S.W.Heinzman and B.Ganem, J.Am.Chem.Soc. 104 (1982) 6801

249 M.Nishiki, H.Miyataka, Y.Niino, N.Mitsuo and T.Satoh, Tetrahedron Lett. 23 (1982) 193

250 S.L.Grundy and P.M.Maitlis, J.C.S.Chem.Commun., (1982) 379

251 A.M.Caporusso, G.Giacomelli and L.Lardicci, J.Org.Chem. 47 (1982) 4640

252 E.Keinan and P.A.Gleize, Tetrahedron Lett. 23 (1982) 477

253 P.Four and F.Guibe, Tetrahedron Lett. 23 (1982) 1825

254 E.Keinan and N.Greenspoon, Tetrahedron Lett. 23 (1982) 241

255 R.O.Hutchins and K.Learn, J.Org.Chem. 47 (1982) 4380

256 M.F.Semmelhack and R.N.Misra, J.Org.Chem. 47 (1982) 2469

257 I.Ojima and T.Kogure, Organometallics 1 (1982) 1390

258 T.Kogure and I.Ojima, J.Organometal.Chem. 234 (1982) 249

259 G.Göndös and J.C.Orr, J.C.S.Chem.Commun. (1982) 1238

260 X.Lu, J.Sun and X.Tao, Synthesis (1982) 185

261 D.Mansuy, M.Pontecave and J.-P.Battioni, J.C.S.Chem.Commun. (1982) 317

262 M.Nitta and T.Kobayashi, Tetrahedron Lett. 23 (1982) 3925

263 J.L.Graff and M.S.Wrighton, Inorg.Chim.Acta 63 (1982) 63

264 A.T.Poulos, G.S.Hammono and M.E.Burton, Photochem. Photobiol. 34 (1981) 169

265 E.Tsuchida, H.Nishide, N.Shimidzu, A.Yamada, H.Kaneko and Y.Kurimura, Makromol.Chem. Rapid Commun. 2 (1981) 621

266 M.Forster and R.E.Hester, Chem.Phys.Lett. 85 (1982) 287

267 Y.Kurimura and K.Katsumata, Bull.Chem.Soc.Jpn. 55 (1982) 2560

268 M.Tezuka, T.Yajima, A.Tsuchiya, Y.Matsumoto, Y.Uchida and M.Hidai, J.Am.Chem.Soc. 104 (1982) 6834

269 K.Tanaka, Y.Imasaka, M.Tanaka, M.Honjo and T.Tanaka , J.Am. Chem.Soc. 104 (1982) 4258

270 R.Wolf and E.Steckhan, J.Electroanal.Chem.Interfacial Electrochem. 130 (1981) 367

271 F.Fournier, J.Berthelot and P.L.Pascal, Seances Acad.Sci. Ser 2, 294 (1982) 849; CA 97 (1982) 100495

272 M.Hronec and J.Ilavsky, J.Catal. 78 (1982) 465

273 V.V.Antonova, A.M.Bespalova and B.F.Ustavshchikov, Zh.Org. Khim. 18 (1982) 1313

274 V.A.Kudryashov, M.N.Manakov and Yu.N.Bogoslovskii, Neftekhimija 21 (1981) 705

275 S.V.Krylova, L.I.Shcherbak and N.I.Mitskievich, Vestsi Akad.Navuk BSSR,Ser.Khim.Navuk (1982) 21; CA 97 (1982) 126986

276 S.P.Prokopchuk, S.S.Abadzhev and R.S.Yakhnitskii, Visn. L'viv Politekh.Inst. 163 (1982) 39; CA 97 (1982) 126992

277 M.N.Fedorishcheva, T.G.Kosmacheva, I.I.Korsak, V.E.Agabekov and N.I.Mitskevich, Vestsi Akad. Navuk BSSR, Ser.Khim. Navuk (1981) 27; CA 96 (1982) 19621

278 M.I.Dayan, I.D.Kushina, Yu.A.Pazdersi, V.A.Bryukhovetskii and S.S.Levus, Prom.-st. Arm. (1981) N$^{o}$ 10, 32; CA 96 (1982) 122163

279 R.A.Galimov, I.M.Kuznetsova and N.M.Lebedeva, Azerb.Khim.Zh. (1981) N$^{o}$ 4, 41; CA 96 (1982) 199038

280 M.U.Fedurtsa and S.S.Abadzhev, Ukr.Khim.Zh. (Russ.Ed.) 48 (1982) 266; CA 97 (1982) 5747

281 M.Gebler, J.Inorg.Nucl.Chem. 43 (1981) 2759

282 T.Miura, K.Shibata, T.Sawaya and M.Kimura, Chem.Pharm.Bull. 30 (1982) 67

283 X.Wang, M.Zhang, H.Hong, L.Guo, Q.Lu, T.Xtong, G.Zha and G.Li, Cuihua Xuebao 2 (1981) 323; CA 96 (1982) 84888

284 X.Wang, M.Zhang, H.Hong, G.Zha and G.Li, Fundam.Res.Organomet.Chem.,Proc.China-Jpn-U.S.Trilateral Semin.Organomet. Chem., 1st. (1980) 723; CA 97 (1982) 71765

285 B.Ya.Ladygin and N.N.Fedyaeva, Neftekhimiya 22 (1982) 237

286 B.G.Freidin and A.L.Perkel, Zh.Priklad.Khim. (Leningrad) 54 (1981) 2733

287 R.Wang, M.Xie and R.Wang, Huagong Xuebao (1982) 50; CA 97 (1982) 55071

288 E.L.Gershanova, M.M.Mogilevich, M.F.Sorokin, G.V.Klimov and V.D.Sukhov, Deposited Doc. (1981) VINITI 2801; CA 97 (1982) 126975

289 L.V.Shibaeva, N.G.Ariko, Yu.I.Gudimenko and N.I.Mitskevich Vestsi Akad.Navuk BSSR, Ser.Khim.Navuk (1982) 40; CA 97 (1982) 215602

290 E.A.Efanova, K.E.Kharlampidi and N.M.Lebedeva, Neftekhimiya 22 (1982) 242

291 A.Zombeck, D.E.Hamilton and R.S.Drago, J.Am.Chem.Soc. 104 (1982) 6782

292 M.T.Atlay, M.Preece, G.Strukul and B.R.James, J.C.S.Chem. Commun., (1982) 406

293 M.Cihova, J.Vojtko, M.Hrusovsky and P.Marek, Petrochemia 21 (1981) 72; CA 96 (1982) 103574

294 J.Tsuji, H.Nagashima and K.Hori, Tetrahedron Lett. 23 (1982) 2679

295 H.Nagashima, K.Sakai and J.Tsuji, Chem.Lett. (1982) 859

296 W.K.Wan, K.Zaw and P.M.Henry, J.Mol.Catal. 16 (1982) 81

297 A.V.Devekki, D.V.Mushenko and V.S.Fedorov, Zh.Org.Khim. 17 (1981) 2519

298 S.M.Brailovski, L.Elfterin. O.N.Chernysheva and A.P.Belov Kinet.Katal. 23 (1982) 54

299 J.Muzart, P.Pale and J.P.Pete, Tetrahedron Lett. 23 (1982) 3577

300 I.A.Krylov, I.Yu.Litvintsev, V.N.Sapunov and N.N.Lebedev Kinet.Katal. 23 (1982) 853

301 I.A.Krylov, M.Yu.Baevskii, I.Yu.Litvintsev, V.N.Sapunov and N.N.Lebedev, Kinet.Katal. 23 (1982) 858

302 S.Ito, K.Inoue and M.Matsumoto, J.Am.Chem.Soc. 104 (1982) 6450

302a S.Futamura, H.Ohta and Y.Kamiya, Chem.Lett. (1982) 381

303 A.Heuman, F.Chauvet and B.Waegell, Tetrahedron Lett. 23 (1982) 2767

304 M.A.Andrews and C.W.F.Cheng, J.Am.Chem.Soc. 104 (1982) 4268

305 D.G.Batyr, I.M.Reibel and A.F.Sandu, Azerb.Khim.Zh. (1981) N$^o$ 4, 69 ; CA 96 (1982) 180494

306 W.Sawodny, R.Grünes and H.Reitzle, Angew.Chem. 94 (1982) 803

307 J.-M.Maissant, C.Bouchoule and M.Blanchard, J.Mol.Catal. 14 (1982) 333

308 A.Ya.Yuffa, U.V.Berentsveig, A.V.Kudryavtsev and G.V.Lisichkin, Kinet.Katal. 22 (1981) 1469

309 V.F.Nazimok, V.N.Kulakov and T.A.Simonova, Azerb.Khim.Zh (1981) N$^o$ 4, 101; CA 96 (1982) 180498

310 M.Hronec and J.Ilavsky, Ind.Eng.Chem.,Prod.Res.Dev. 21 (1982) 455

311 K.Shimizu, K.Kizawa, T.Yoshimoto and J.Imamura, Sekiyu Gakkaishi 25 (1982) 7; CA 96 (1982) 122333

312 J.Koshitani, T.Kado, Y.Ueno and T.Yoshida, Bull.Chem.Soc. Jpn. 55 (1982) 1931

313 J.Koshitani, T.Kado, Y.Ueno and T.Yoshida, J.Org.Chem. 47 (1982) 2879

314 V.V.Berentsveig, O.E.Dotsenko, A.I.Kokorin, V.D.Kopylova and E.L.Frumkina Izv.Akad.Nauk SSSR, Ser.Khim. (1982) 2211

315 M.V.Nesterov, V.A.Ivanov, V.M.Potekhin and A.U.Kazannikova Azerb.Khim.Zh. (1981) N$^o$ 4, 48-50; CA 96 (1982) 180492

316 S.Shinkai, Y.Ishikawa and O.Manabe, Chem.Lett. (1982) 809

317 E.Papaconstantinou, J.C.S.Chem.Commun. (1982) 12

318 V.P.Tret'yakov, G.P.Zimtseva, E.S.Rudakov and A.V.Bogdanov Kinet.Katal. 23 (1982) 247

319 V.P.Tret'yakov, G.P.Zimtseva, E.S.Rudakov and A.U.Bogdanov Kinet.Catal.Lett. 19 (1982) 263

320 N.I.Jonescu and D.Popescu, Rev.Roum.Chim. 27 (1982) 481; CA 97 (1982) 23092

321 Y.Tatsuno, M.Tatsuda and S.Otsuka, J.C.S.Chem.Commun. (1982) 1100

322 M.Matsumoto and K.Kuroda, J.Am.Chem.Soc. 104 (1982) 1433

323 C.Bied-Charreton, M.Frostin-Rio, D.Puyol, A.Gaudemer, R.Audebert and J.P.Idoux, J.Mol.Catal. 16 (1982) 335

324 A.N.Astanina, A.F.Gamidov, A.P.Rudenko and G.L.Smirnova Azerb. Khim. Zh. (1981) 20; CA 96 (1982) 92398

325 K.Ohkubo, K.Miyata and S.Sakaki, J.Mol.Catal. 17 (1982) 85

326 T.Funabiki, T.Sugimoto, S.Yoshida, Chem.Lett. (1982) 1097

327 K.Seguchi and S.Hirota, Chem.Lett. (1982) 385

328 Yu.I.Pyatnitskii, V.M.Vorotyntsev, O.Biryukovich and E.P. Kuznetsova, Kinet.Katal. 23 (1982) 608

329 D.G.Brown and W.J.Hughes, Z.Naturforsch 36B (1981) 1324

330 H.Nishide, T.Minakata and E.Tsuchida, J.Mol.Catal. 15 (1982) 327

331 R.J.Radel, J.M.Sullivan and J.D.Hatfield, Ind.Eng.Chem.Prod. Res.Dev. 21 (1982) 566

332 H.Egawa, T.Nonaka and N.Kozakura, Bull.Chem.Soc.Jpn. 55 (1982) 3536

333 P.Capdevielle and M.Maumy, Tetrahedron Lett. 23 (1982) 1573

334 P.Capdeville and M.Maumy, Tetrahedron Lett. 23 (1982) 1577

335 G.J.Lambert, R.P.Duffley, H.C.Dalzell and R.K.Razdan , J.Org.Chem. 47 (1982) 3350

336 I.Apostol, J.Haber, T.Mlodnicka and J.Poltowicz, J.Mol.Catal. 14 (1982) 197

337 C.Jallabert, C.Lapinte and H.Riviere, J.Mol.Catal. 14 (1982) 75

338 P.Lederer, S.Lunak, E.Macova and J.Veprek-Siska, Collect. Czech.Chem.Commun. 47 (1982) 392

339 N.M.Lebedeva, L.D.Marus and L.I.Kornilova, Khim.Tekhnol. Pererab.Nefti Gaza (1981) 8; CA 97 (1982) 181522

340 O.P.Dmitrieva, G.N.Supichenko, V.E.Agabekov, I.I.Korsak and N.I.Mitskevich, Vestsi Akad.Navuk BSSR, Ser.Khim.Navuk (1982) N$^{O}$1, 22; CA 96 (1982) 180464

341 J.Muzart and J.P.Pete, J.Mol.Catal. 15 (1982) 373

342 T.Nakayama, E.Nakamura and K.Koguchi, Nippon Kagaku Kaishi (1982) 472; CA 96 (1982) 217010

343 N.E.Davidenko, S.A.Borisenkova and A.P.Rudenko, Vestn.Mosk. Univ.Ser.2:Khim. 23 (1982) 269; CA 97 (1982) 55096

344 D.M.Wagnerova, J.Blanck and J.Veprek-Siska, Collect.Czech. Chem.Commun. 47 (1982) 755

345 K.Mikova, V.Kyzlink and A.Heinzova, Sb.Vys.Sk.Chem.-Technol. Praze, Potraviny E52 (1981) 15; CA 97 (1982) 90541

346 Yu.P.Zhukov, R.B.Suitych, N.N.Rzhevskaja, O.P.Jablonski and A.V.Bondarenko, Zh.Org.Khim. 18 (1982) 78

347 I.M.Krip and A.I.Klyuchkivskii, Visn.L'viv.Politekh.Inst. 163 (1982) 22; CA 97 (1982) 126774

348 S.Sano and Y.Sugiura, J.C.S.Chem.Commun. (1982) 750

349 D.Mansuy, P.Battioni and J.P.Mahy, J.Am.Chem.Soc. 104 (1982) 4487

350 S.Cenini, F.Porta and M.Pizzotti, J.Mol.Catal. 15 (1982) 297

351 A.M.Bespalova, V.V.Antonova, I.A.Ershova and B.F.Ustavshchikov, Osnovn.Org.Sint.Neftekhim. 13 (1980) 61; CA 97 (1982) 162104

352 S.Németh and L.Simándi, J.Mol.Catal. 14 (1982) 87

353 S.Németh and L.Simándi, J.Mol.Catal. 14 (1982) 241

354 K.A.Askarov, E.V.Bystritskaya, R.V.Tashmatova, V.Onishchenko, B.R.Smirnov, G.G.Tsoi and N.S.Enykolopyan Dokl.Akad.Nauk, SSSR 262 (1982) 635

355 A.Inada, Y.Nakamura and Y.Morita, Chem.Pharm.Bull. 30 (1982) 1041; CA 97 (1982) 109612

356 A.Nishinaga, H.Tomita, M.Oda and T.Matsuura, Tetrahedron Lett. 23 (1982) 339

357 A.Nishinaga, T.Shimizu, Y.Toyoda, T.Matsuura and K.Hirotsu, J.Org.Chem. 47 (1982) 2278

358 S.Németh and L.I.Simándi, Inorg.Chim.Acta 64 (1982) L21

359 K.Kaneda, T.Itoh, N.Kii, K.Jutsukawa and S.Teranishi J.Mol.Catal. 15 (1982) 349

360 T.Kajimoto, H.Takahashi and H.Tsuji, Bull.Chem.Soc.Jpn. 55 (1982) 3673

361 É.Balogh-Hergovich, G.Bodnár and G.Speier, Acta Chim.Acad. Sci.Hung. 108 (1981) 37

362 É.Balogh-Hergovich, G.Speier and Z.Tyeklár, Synthesis (1982) 731

363 J.O.Cabral, M.F.Cabral, M.G.B.Drew, F.S.Esho and S.M. Nelson, J.C.S.Chem.Commun. (1982) 1068

364 N.Ueyama, E.Kamada and A.Nakamura, Chem.Lett. (1982) 947

365 D.M.Roundhill, M.K.Dickson, N.S.Dixit and B.P.Sudha-Dixit Adv.Chem.Ser. 196 (1982) 291

366 A.Skorobogaty and T.D.Smith, J.Mol.Catal. 16 (1982) 131

367 T.A.Anan'eva, G.F.Titova and V.F.Borodkin, Izv.Vyssh. Uchebn.Zaved.,Khim.Khim.Tekhnol 25 (1982) 706; CA 97 (1982) 144092

368 O.Yamauchi and H.Seki, Chem.Lett. (1982) 1241

369 T.U.Shchedrinskaya, A.A.Leichenko and M.N.Volkov, Zh.Org. Khim. 17 (1981) 2177

370 N.P.Belous, F.F.Shcherbina and D.N.Tmenov, Ukr.Khim.Zh. (Russ.Ed.) 47 (1981) 1252; CA 96 (1982) 84876

371 I.V.Spirina, V.N.Alyasov, V.N.Glushakova, N.A.Skorodumova, V.P.Sergeeva, N.V.Balakshina, V.P.Maslennikov, Y.A. Aleksandrov and G.A.Razuvaev, Zh.Org.Khim. 18 (1982) 1796

372 L.N. Arzamaskova, A.V.Romanenko and Yu.I.Ermakov, Kinet. Katal. 22 (1981) 1438

373 L.N.Arzamaskova, A.V.Romanenko and Yu.I.Ermakov, Kinet. Katal. 22 (1981) 1186

374 B.C.Schardt, F.J.Hollander and C.L.Hill, J.Am.Chem.Soc. 104 (1982) 3964

375 E.S.Rudakov, L.K.Vol'kova, V.P.Tret'yakov and V.V. Zamashchikov, Kinet.Katal. 23 (1982) 26

376 S.Tamagaki, K.Hotta and W.Tagaki, Chem.Lett. (1982) 651

377 M.A.Brook, L.Castle, J.R.L.Smith, R.Higgins and K.P.Morris J.C.S.Perkin Trans.II (1982) 687

378 A.M.Khenin and A.A.Steinman, Kinet.Katal. 23 (1982) 219

379 D.Mansuy, J.-F.Bartoli and M.Momenteau, Tetrahedron Lett. 23 (1982) 2781

380 P.Müller and J.Godoy, Helv.Chim.Acta 64 (1981) 2531

381 P.Müller and J.Godoy, Tetrahedron Lett. 23 (1982) 3661

382 S.Uemura and S.RPatil, Tetrahedron Lett. 23 (1982) 4353

382a S.Uemura and S.R.Patil, Chem.Lett (1982) 1743

383 S.Uemura, S.Fukuzawa, A.Toshimitsu and M.Okano, Tetrahedron Lett. 23 (1982) 87

384 E.S.Rudakov and L.K.Volkova, Dokl.Akad.Nauk SSSR, 263 (1982) 647

385 Ya.A.Dorfman, Zh.Fiz.Khim. 55 (1981) 2793

386 F.Di Furia, H.Modena, R.Curci, S.J.Bachofer, J.O.Edwards and M.Pomerantz, J.Mol.Catal. 14 (1982) 219

387 A.S.Narula, Tetrahedron Lett. 23 (1982) 5579

388 D.V.Banthorpe and S.E.Barrow, Chem.Ind. (London), (1981) 502

389 C.E.Chapin, E.F.Twohig, L.D.Keys and K.M.Gorski, J.Appl. Polym,Sci. 27 (1982) 811

390 M.Isobe, M.Kitamura, S.Mio and T.Goto, Tetrahedron Lett. 23 (1982) 221

391 L.A.Reed, Y.Ito, S.Masamune and K.B.Sharpless, J.Am.Chem. Soc. 104 (1982) 6468

392 K.C.Nicolaou and J.Uenishi, J.C.S.Chem.Commun. (1982) 1292

393 W.H.Rastetter, J.Adams, J.Bordner, Tetrahedron Lett. 23 (1982) 1319

394 R.D.Wood and B.Ganem, Tetrahedron Lett. 23 (1982) 707

395 L.I.Simándi, É.Záhonyi-Budó and J.Bodnár, Inorg.Chim. Acta 65 (1982) L181

396 A.P.Filippov, G.A.Konishevskaya and V.M.Beousov , Kinet. Katal. 23 (1982) 346

397 Sh.Liu and B.Yu, Cuihua Xuebao 2 (1981) 229; CA 96 (1982) 209724

398 U.M.Dzhemilev, R.N.Fakhretdinov, A.G.Telin, G.A.Tolstikov, D.V.Amirkhanov and V.P.Krivonogov, Khim.Prir.Soedin. (1981) 650; CA 96 (1982) 85346

399 S.B.Grinenko, V.M.Belousov, L.A.Oshin, G.A.Shakhovtseva, N.I.Kovtyukhova, A.P.Filippov and K.B.Yatsimirskii, Dokl. Akad.Nauk SSSR, 263 (1982) 1395

400 V.D.Vardanyan, I.Yu.Litvintsev, U.N.Sapunov, A.G.Komarov and T.T.Avakyan, Arm.Khim.Zh. 35 (1982) 141; CA 97 (1982) 38295

401 A.O.Kolmakov, V.M.Fomin, T.N.Aizenshtadt and Yu.A. Aleksandrov, Zh.Obshch.Khim. 51 (1981) 2805

402 Ch.Ch.Su, Ch.H.Ueng, W.H.Lin, M.J.Gi and K.H.Lii, Proc. Natl.Sci.Counc.Rep.China, Part B. 6 (1982) 45; CA 96 (1982) 180230

403 M.B.Groen and F.J.Zeelen, Tetrahedron Lett. 23 (1982) 3611

404 M.Inoue, Y.Itoi, S.Enomoto and Y.Watanabe, Chem Lett. (1982) 1375

405 E.Guilmet and B.Meunier, Tetrahedron Lett. 23 (1982) 2449

406 S.E.Diamond, F.Mares, A.Szalkiewicz, D.A.Muccigrosso and J.P.Solar, J.Am.Chem.Soc. 104 (1982) 4266

407 J.R.L.Smith and P.R.Sleath, J.C.S.Perkin Trans.II (1982) 1009

408 M.W.Nee and T.C.Bruice, J.Am.Chem.Soc. 104 (1982) 6123

409 Y.Masuyama, M.Usukura and Y.Kurusu, Chem.Lett. (1982) 1951

410 M.Barteri and B.Pispisa, Biopolymers 21 (1982) 1093

411 M.Barteri and B.Pispisa, J.C.S.Faraday Trans. I, 78 (1982) 2085

412 S.Shinoda, N.Inove, K.Takita and Y.Saito, Inorg.Chim. Acta 65 (1982) L21

413 S.C.Pati and B.R.Dev, Rev.Roum.Chim. 27 (1982) 523; CA 97 (1982) 23093

414 S.C.Pati and M.Panda, Bull.Soc.Chim.Belg. 91 (1982) 271

415 R.Singh and S.M.Singh, Ann.Soc.Sci.Bruxelles,Ser.1, 95 (1981) 251; CA 97 (1982) 23094

416 K.Behari, R.S.Shukla, R.K.Dwivedi, N.N.Pandey, Oxid. Commun 2 (1981) 63; CA 97 (1982) 215270

417 H.S.Singh, K.C.Tiwari and S.M.Singh, Indian J.Chem, Sect A 21A (1982) 520; CA (1982) 181505

418 R.K.Dwivedi, H.Narayan and K.Behari, J.Inorg.Nucl.Chem. 43 (1981) 2893

419 N.Nath, L.P.Singh and R.P.Singh, J.Indian Chem.Soc. 58 (1981) 1204

420 M.Kimura, A.Kobayashi and K.Boku, Bull.Chem.Soc.Jpn. 55 (1982) 2068

421 A.Z.Muradov and A.A.Yasnikov, Dopov.Akad.Nauk Ukr. RSR, Ser.B: Geol.Khim.Biol.Nauki (1982) 3, 39; CA 97 (1982) 12482

422 S.P.Srivastava, A.Kumar and V.K.Gupta, Rev.Roum.Chim. 26 (1981) 939

423 J.A.Litwin, Acta Histochem. 71 (1982) 111; CA 97 (1982) 106400

424 R.C.Acharya, N.K.Saran, S.R.Rao and M.N.Das, Int.J.Chem. Kinet. 14 (1982) 143

425 Y.Nakayama, Y.Sanemitsu and H.Yoshioka, Tetrahedron Lett. 24 (1982) 2499

426 O.S.Fedorova, S.E.Olkin and V.M.Berdnikov, Z.Phys.Chem. (Leipzig) 263 (1982) 529

427 Y.Ogata and K.Tanaka, Can.J.Chem. 60 (1982) 848

428 O.Bortolini, F.Di Furia and G.Modena, J.Mol.Catal. 16 (1982) 61

429 O.Bortolini, F.Di Furia and G.Modena, J.Mol.Catal. 16 (1982) 69

430 O.Bortolini, C.Campello, F.Di Furia and G.Modena, J.Mol. Catal. 14 (1982) 63

431 O.Bortolini, F.Di Furia and G.Modena, J.Mol.Catal. 14 (1982) 53

432 W.Ando, R.Tajima and T.Takata, Tetrahedron Lett. 23 (1982) 1685

433 S.Oae, Y.Watanabe and K.Fujimori, Tetrahedron Lett. 23 (1982) 1184

434 E.S.Rudakov, N.A.Tishchenko, V.P.Kukhar and U.F.Baklan, Dopov.Akad.Nauk.Ukr.RSR.Ser.B: Geol.Khim.Biol.Nauki (1982) 54; CA 97 (1982) 126755

435 T.K.Chakraborty and S.Chandrasekaran, Org.Prep.Proced. Int. 14 (1982) 362; CA 97 (1982) 215073

436 M.V.De Martinez, F.G.De Vendetti, I.J.S.De Fenik and C.A. N.Catalan, An.Assoc.Quim. Argent. 70 (1982) 137; CA 96 (1982) 218042

437 D.M.Walba and G.S.Stoudt, Tetrahedron Lett. 23 (1982) 727

438 L.K.Volkova, Yu.V.Goletii, G.V.Lyubimova, E.S.Rudakov, V.P.Tret'yakov and A.E.Shilov, Izv.Akad.Nauk SSSR,Ser. Khim. (1982) 1654

439 J.Burkhard, P.Jakoubek and L.Vódicka, Sb.Vys.Sk.Chem.-Technol.Praze, Technol.Paliv, D44 (1981) 157; CA 97 (1982) 181811

440 Z.S.Makarova and I.B.Repinskaya, Zh.Org.Khim. 18 (1982) 1022

441 D.G.Lee, S.E.Lamb and V.S.Chang, Org.Synth. 60 (1981) 11

442 N.Garti and E.Auni, Colloids Surf. 4 (1982) 33

443 D.G.Lee and K.C.Brown, J.Am.Chem.Soc. 104 (1982) 5076

444 A.Z.Kreindlin and M.I.Rybinskaya, Izv.Akad.Nauk SSSR, Ser.Khim. (1982) 174

445 S.Kumar and P.C.Mathur, Chem.Prum. 31 (1981) 359; CA 96 (1982) 51595

446 M.S.Thompson and T.J.Meyer, J.Am.Chem.Soc. 104 (1982) 5070

447 M.Schröder and E.C.Constable, J.C.S.Chem.Commun. (1982) 734

448 L.Joensson, Acta Chem.Scand., B 35 (1981) 683

449 M.Puutio and P.O.I.Virtanen, Finn.Chem.Lett. (1981) N$^{o}$7-8, 87; CA 96 (1982) 122022

450 J.E.Hila, M.Tsini-Tsamis, M.Hamon and J.P.Delacroix Analusis 10 (1982) 220; CA 97 (1982) 78767

451 J.Herscovici, M.-J.Ergon and K.Antonakis, J.C.S.Perkin Trans.I (1982) 1967

452 T.T.Minasyan, F.S.Kinoyan and Sh.O.Badanyan, Arm.Khim.Zh. 35 (1982) 579; CA 97 (1982) 215481

453 S.U.Kulkarni, C.G.Rao, V.D.Patil, Heterocycles 18 (1982) 321

454 Y.Ishikawa, M.Yoshida and T.Ando, Osaka Kogyo Gijutsu Shikensho Kiho 33 (1982) 1; CA 97 (1982) 38533

455 F.S.Guziec and F.A.Luzzio, J.Org.Chem. 47 (1982) 1787

456 P.C.Samal, S.Ch.D.Rao and S.N.Mahapatro, Curr.Sci. 51 (1982) 41; CA 97 (1982) 197666

457 M.Matsuda, N.Yasuda and W.Yano, Kiyo-Suzuka Kogyo Koto Senmon Gakko 15 (1982) 217; CA 97 (1982) 71903

458 J.M.J.Frechet, P.Darling and M.J.Farall, Polym.Prepr.Am.Chem.Soc.Div.Polym.Chem. 21 (1980) 272

459 J.Holecek, K.Handlir and M.Nadvornik, Collect.Czech.Chem.Commun. 47 (1982) 562

460 I.N.Pinchuk, V.F.Chuvaev, N.S.Ovchinnikova, L.T.Zhuravlev and V.I.Spitsyn, Izv.Akad.Nauk SSSR, Ser.Khim. (1982) 798

461 J.R.Darwent, J.C.S.Chem.Commun. (1982) 798

462 P.N.Pande, H.L.Gupta, S.C.Ameta and T.C.Sharma, Acta Phys. Chem. 27 (1981) 125; CA 96 (1982) 163062

463 G.V.Rao, K.Ch.Rajanna and P.K.Saiprakash, Z.Phys.Chem. (Leipzig) 263 (1982) 622

464 F.Freeman, D.K.Lin and G.R.Moore, J.Org.Chem. 47 (1982) 56

465 N.A.Noureldin and D.G.Lee, J.Org.Chem. 47 (1982) 2790

466 B.L.Seong and M.H.Han, Chem.Lett. (1982) 627

467 A.Cornelis, P.Y.Herzé and P.Laszlo, Tetrahedron Lett. 23 (1982) 5035

468 A.G.Milaev, V.B.Panov and O.Yu.Okhlobystin, Zh.Obshch. Khim. 51 (1981) 2715

469 M.S.Thompson and T.J.Meyer, J.Am.Chem.Soc. 104 (1982) 4106

470 T.Morimoto and M.Hirano, J.C.S.Perkin Trans.II (1982) 1087

471 M.Kimura, M.Yamamoto-Tsuruta and S.Yamabe, J.C.S. Dalton Trans. (1982) 423

472 D.Fox and C.F.Wells, J.C.S.Faraday Trans.I, 78 (1982) 1525

473 D.Fox and C.F.Wells, J.C.S.Faraday Trans.I, 78 (1982) 2929

474 J.C.Brodovitch, A.McAuley and T.Oswald, Inorg.Chem. 21 (1982) 3442

475 H.Yamamoto and T.Hayakawa, Int.J.Biol.Macromol. 4 (1982) 116

476 A.Kumar, J.Phys.Chem. 86 (1982) 1674

477 R.S.Macomber, J.Org.Chem. 47 (1982) 2481

478 T.R.Prasad, B.S.Ram and T.N.Rao, Curr.Sci. 51 (1982) 749; CA 97 (1982) 162115

479 K.E.Rittle, C.F.Homnick, G.S.Ponticello and B.E.Evans, J.Org.Chem. 47 (1982) 3016

480 A.V.Stachulski, Tetrahedron Lett. 23 (1982) 3789

481 N.Kornblum, A.S.Erickson, W.J.Kelly and B.Henggeler, J. Org.Chem. 47 (1982) 4534

482 J.H.Clark and D.G.Cork, J.C.S.Chem.Commun. (1982) 635

483 R.Nesi, S.Chimichi, F.De Sio, R.Pepino and P.Tedeschi, Tetrahedron Lett 23 (1982) 4397

484 H.Firouzabadi, B.Vessal and M.Naderi, Tetrahedron Lett. 23 (1982) 1847

485 S.W.Pelletier, J.A.Glinski and N.V.Mody, J.Am.Chem.Soc. 104 (1982) 4676

486 T.S.Boiko, O.M.Grishin and A.A.Yasnikov, Ukr.Khim.Zh. (Russ.Ed.) 48 (1982) 390; CA 97 (1982) 5596

487 N.Tsubokawa, N.Takeda and Y.Sone, Bull.Chem.Soc.Jpn. 55 (1982) 3541

488 T.Fujii, T.Hiraga and M.Ohba, Chem.Pharm. Bull. 29 (1981) 2503

489 T.Itahara, H.Ouya and K.Kozono, Bull.Chem.Soc.Jpn. 55 (1982) 3861

490 R.Sugimoto, H.Suzuki, Y.Moro-Oka and T.Ikawa, Chem.Lett. (1982) 1863

491 E.F.de A.Neves, W.Polito, W.L.Moraes and D.W.Franco, Talanta 28 (1981) 867

492 D.G.Lee and C.F.Sebastian, Can.J.Chem. 59 (1981) 2776, 2780

493 A.K.Bhattacharjee and M.K.Mahanti, Int.J.Chem.Kinet. 14 (1982) 1113

494 T.V.Lee and J.Toczek, Tetrahedron Lett. 23 (1982) 2917