TRANSITION METALS IN ORGANIC SYNTHESIS: HYDROFORMYLATION, REDUCTION AND OXIDATION

ANNUAL SURVEY COVERING THE YEAR 1983

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CONTENTS

Introduction

The papers in this survey 1983 have been largely grouped by reaction type and not by the transition metal complexes used in the organic transformations. 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

Extended Hückel calculations of various intermediates for the reaction of olefins with $MoO(O_2)_2L_2$ confirm the viability of olefin coordination and metallocycle formation *trans* to the oxo ligand.

Epoxide is eliminated from this metallocyclic unit by a concerted process [1]. The reactivity of C-H bonds for homolytic splitting in cumene, p-cymene, p- and m-diisopropylbenzene has been determined on the basis of quantum chemical calculations. The reactivity of these hydrocarbons towards hydroperoxidation by O_2 was measured at 115°C in the presence of Fe and Mn alkanoates, various free radical initiators and Fe or Sb polyphtalocyanines. The reactivity sequence determined experimentally agrees with the theoretically calculated one only in the case of the phtalocyanines [2].

II. Hydroformylation and Related Reactions of CO

1. Hydrogenation of CO to Hydrocarbons and Oxygen-containing Organic Compounds

The homogeneous hydrogenation of CO with $Ir_4(CO)_{12}$ catalyst in molten $AlCl_3$-NaCl has been kinetically examined in a singlepass flow reactor and a continuous recycle apparatus. The principal products were methane, ethane, and MeCl. Experimental evidence suggests that MeCl is the primary product of the reaction [3]. Complexes of Mo(III) with pyrocatechol catalyze the electrochemical reduction of CO on a Hg cathode in aqueous solution. Reaction products are C_1 - C_4 hydrocarbons, additionally H_2 is evolved [4].

Carbon monoxide is hydrogenated to methanol, ethylene glycol and ethanol by a catalyst composed of Ru carbonyls and iodine. The chemistry of this system has now been investigated in detail. Spectroscopic studies show, that $HRu_3(CO)_{11}^-$ and $Ru(CO)_3I_3^-$ are mainly present in the reaction mixture but kinetic evidence suggests that the reaction between $HRu(CO)_4^-$ and $Ru(CO)_2I_2$ is the critical step of the catalytic cycle [5]. Similar catalyst systems obtained from $Ru_3(CO)_{12}$ and HI in a phosphine oxide solvent are unusually selective for ethanol at 180 - 250°C and 300 - 870 bar. Catalytic activity is associated with $Ru(CO)_3I_3^-$ and $HRu_3(CO)_{11}^-$ complexes in the reaction mixture present as their R_3POH^+ protonated phosphine oxide salts. Most of the ethanol is formed from methanol but some may be directly formed from CO and H_2 [6].

Ethylene glycol and its monoalkyl ether derivatives are formed from synthesis gas (CO/H_2 = 1/1) at relatively low pressures (300-400 bar) at 220°C if a mixed Ru-Rh catalyst system is used in a low-melting point quaternary phosphonium salt as solvent. Ru is the metal principally responsible for glycol formation, Rh increases glycol productivity up to a Rh:Ru ratio of 1:1. A mixed cluster formulated as $Ru_2Rh(CO)_{12}$ has been isolated from the reaction mixture [7]. Ethylene glycol diacetate was formed in high selectivity from CO and H_2 at 230°C and 1000 bar in the presence of a homogeneous catalyst system composed of Ru and Rh complexes and Et_3N. The Ru:Rh ratio was around 10:1 and acetic acid was used as solvent. Spectroscopic evidence did not support the presence of mixed-metal species [8]. $Ru_3(CO)_{12}$ supported on MgO yields significant amounts of MeOH and EtOH from synthesis gas at 200 - 225°C. After catalysis the anionic cluster $Ru_6C(CO)_{16}^{2-}$ was identified on the catalyst. The oxygenate selectivity is suggested to be a result of the presence of intact metal clusters on the surface [9].

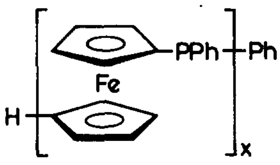
2. Hydroformylation

a) Co Catalysts

The kinetics of the main and side reactions in the hydroformylation of acrylonitrile to β-cyanopropionaldehyde in MeOH were studied. The reactions were zero order in nitrile and first order in Co carbonyl catalyst [10]. The characteristics of a reactor for the hydroformylation of acrylonitrile have been determined by calculations and experimentally [11]. Removal of Co catalysts from products of hydroformylation was carried out by treatment with CO_2 at 60-110°C and 5-10 bar [12].

The hydroformylation of 1,1-diphenylethylene with $Rh_2(CO)_4Cl_2$ as catalyst yielded 85% aldehyde and 11% hydrogenated product. Under similar conditions but using $Co_2(CO)_8$ as catalyst only 5% of the olefin were hydroformylated whereas 95% were hydrogenated. This suggests that the cobalt-catalyzed reaction is free radical in nature while the Rh-catalyzed reaction involves olefin insertion into the Rh-H bond [13]. Cycloheptatriene can be hydroformylated with a Rh + PPh_3 catalyst mainly to diformylcycloheptanes. With $Co_2(CO)_8$ or Rh carbonyl alone only monoformylcycloheptane is obtained [14]. In the hydroformylation of ethylene with equimolar H_2 + D_2 mixtures and $Rh_4(CO)_{12}$ or $Co_2(CO)_8$ as catalyst precursor about 50% of the propionaldehyde formed was a d_1-product. Since very small H_2/D_2 scrambling occurs this result excludes activation of hydrogen through $M(H_2)$ or $M(H_2)$ olefin complexes [15].

The hydroformylation of propylene trimers has been studied with a $Co_2(CO)_8$ + $(n\text{-}C_{12}H_{25})_3P$ catalyst. Alcohols were obtained with up to 80% selectivity [16]. Cobalt carbonyl complexes containing the oligomeric or polymeric ligands of types (1a,1b) have been prepared and used as catalysts in the hydroformylation of 1-hexene. The results were comparable to those obtained with PPh_3-containing complexes. Consecutive hydrogenation of aldehydes to alcohols was slow and this was attributed to increased tridentate coordination to cobalt [17].



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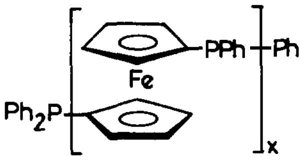


1b

The chelate complex $HCo(CO)_2(Bu_2PCH_2CH_2PBu_2)$ was found to be inactive as a catalyst for the hydroformylation of propene at 180°C. It was slowly transformed, however, under the reaction conditions into an active form. This latter is supposed to be a polynuclear Co carbonyl hydride in which the Co atoms are linked by diphosphine bridges [18]. Hydroformylation of 1-hexene is catalyzed by the polymeric phosphido-bridged complex $[Co(\mu\text{-}PPh_2)(CO)_3]_x$ at 110°C and 90 bar CO + H_2. The activity of this complex is much less than that of $Co_2(CO)_8$ and in addition it is transformed into $Co_2(CO)_6(PHexPh_2)_2$ under the reaction conditions (Hex = C_6H_{13}). This result implies that phosphido-bridged clusters may find only limited usefulness in catalysis because of such irreversible transformations which destroy the polynuclear character of the complex [19].

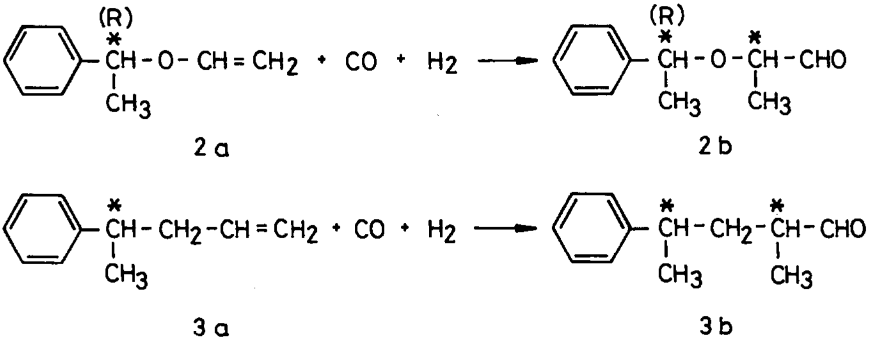
The mixed-metal cluster $Pt_2Co_2(CO)_8(PPh_3)_2$ was found to have a high catalytic activity for hydroformylation of 1-hexene under mild conditions [20]. Clusters of the type $Co_3(CO)_9(S)(LX)$ prepared from $Co_2(CO)_8$ and thioamides were tested as hydroformylation catalysts. Only those clusters were found to be active which possess a $Co(CO)_3$ group which can be liberated under the reaction conditions. Apparently these clusters act merely as storehouses for the release of catalytically active fragments [21].

The photochemical hydroformylation of 1-octane with Co catalysts modified with PBu_3 in MeOH leads under mild conditions (80°C, 80 bar CO + H_2) with $\geq$ 90% selectivity to linear aldehydes. The reaction rate is nearly independent of the Co source (e.g. $Co(OAc)_2$ or $Co_2(CO)_8$). At low pressures hydroesterification is preferred. UV irradiation of Co acetate under hydroformylation conditions leads to rapid reduction of the Co(II) species, thus decreasing the induction period significantly [22].

b) Rh Catalysts

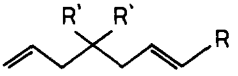
Cocondensation of Rh atoms with cyclodienes at liquid N_2 temperature yields Rh complexes which are at 20-50°C and 70 bar good catalysts for the hydroformylation of these cyclodienes to the corresponding unsaturated monoaldehydes. The catalysts are oily substances and are probably (cyclodienyl)(cyclodiene)rhodium(I) species [23].

In the Rh-catalyzed hydroformylation of the chiral vinyl ether (2a) the diastereoselectivity observed in the formation of the branched aldehyde (2b) is much higher (62%) than that in formation of the aldehyde (3b) from the structurally related olefin (3a)(2%):

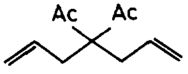


This is the highest diastereoselectivity observed so far during hydroformylation of a chiral olefin with an achiral catalyst [24]. The preparation and characterization of supported liquid phase SLP Rh catalysts for hydroformylation of olefins has been described [25].

Several mono-, di- and triolefins were hydroformylated with $HRh(CO)(PPh_3)_3$ as catalyst at room temperature and atmospheric pressure. Dienes of the type (4) could be selectively hydroformylated at the terminal double bond, 4,4-diacetylhepta-1,6-diene (5) gave a mixture of mono- and dialdehydes. Trienes (6) were transformed into their cyclic adducts (7) prior to hydroformylation and thus selective transformation of the isolated double bond could be achieved. Methylenecyclopentane (8) afforded the terminal aldehyde but methylenecyclobutane (9) was only isomerized to methylcyclobutene [26].



4 (R = Me, CH_2COOEt)



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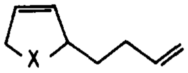
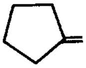


7 (X = S, SO, SO_2)



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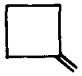

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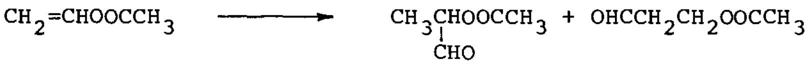
The hydroformylation of vinyl acetate with $HRh(CO)(PPh_3)_3$ as catalyst produces the branched isomer as the main product:



$$CH_2{=}CHOOCCH_3 \longrightarrow \underset{\textstyle CHO}{CH_3CHOOCCH_3} + OHCCH_2CH_2OOCCH_3$$

The ratio of α : β-formyl products increases if the vinyl esters of more bulky acids (e.g. pivalic) are hydroformylated. The activity of the catalyst gradually decreases because of the hydrogenolysis of vinyl acetate to form ethylene and acetic acid (catalyzed by the Rh complex) and the buildup of acetic acid which reacts with the hydridic form of the catalyst [27]:

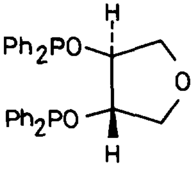
$$CH_2{=}CHOOCCH_3 + H_2 \longrightarrow CH_2{=}CH_2 + CH_3COOH$$

$$HRh(CO)_2(PPh_3)_2 + CH_3COOH \rightleftharpoons Rh(CO)(PPh_3)_2(OOCCH_3) + H_2 + CO$$

The hydroformylation of propylene with $Rh(CO)(PPh_3)(acac)$ as catalyst was studied by high-temperature and high-pressure IR spectroscopy [28]. The activity of the $HRh(CO)(PPh_3)_3$ + PPh_3 hydroformylation catalyst system gradually decreases upon repeated hydroformylation and product distillation. The addition of diphenyl- or di-n-octyl-phosphinous acid improves the stability of the system. It is assumed that the formation of $Rh_2(CO)_2(PPh_3)_2(R_2PO)_2$ is responsible for this effect. This complex is thermally stable and generates $HRh(CO)(PPh_3)_3$ and phosphinous acid when exposed to H_2 [29].

The hydroformylation of hexene-1 with Rh(acac)L_2 L = $P(OPh)_3$ has been studied at 290 K and 1 bar (H_2:CO = 1:1). The formation of the following intermediates has been confirmed by ^1H and ^{31}P NMR and IR spectroscopy: Rh(acac)$(CO)_2L_2$, H_2Rh(acac)L_2 and HRh(acac)(CO)L_2. The interaction of the last species with the olefin is postulated to be the slowest reaction in the system [30]. Unreactive cyclic and branched internal olefins like limonene or 2-methyl-1-hexene are hydroformylated under mild conditions (90°C and 10 bar) in the presence of rhodium catalysts modified with sterically demanding and strongly electron-withdrawing phosphites. Tris o-t-butylphenyl phosphite is an especially favorable ligand [31].

The phosphinite (10) was prepared and used as a ligand with Rh complexes for asymmetric hydrogenation and hydroformylation. In the hydroformylation of vinyl acetate 4-6% optical yields were achieved, in hydrogenation the ligand was less enantioselective than (-)-DIOP (11) [32].



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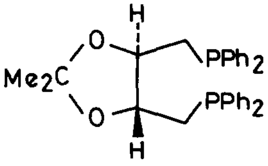
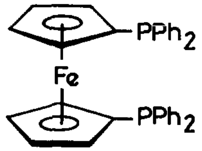


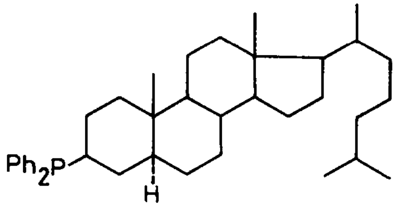
11,(-)-DIOP

Hydroformylation of allyl alcohol was studied using HRh(CO)$(PPh_3)_3$ and its analogs as catalysts. Using the ferrocenyl bisphosphine (12) as ligand > 80% selectivity for $HO(CH_2)_3CHO$ was achieved [33].



12

The hydroformylation of 1-hexene in the presence of HRh(CO)$(PPh_3)_3$+ bidentate phosphine ligand catalysts has been studied. Highest selectivities for linear aldehyde were obtained with DIOP (11) and with trans-1,2-bis(diphenylphosphinoethyl)cyclobutane. For bidentate ligands, the catalyst was postulated to be a dirhodium complex [34]. Two new optically active phosphines (+)-DICOL (13) and (-)-DIOCOL (14) containing steroid groups have been prepared and used as ligands in asymmetric hydrogenation and hydroformylation of olefins catalyzed by rhodium complexes. The bisphosphine DIOCOL provided the higher asymmetric inductions. Optical yields of up to 93% and 34%, respectively, were obtained [35].



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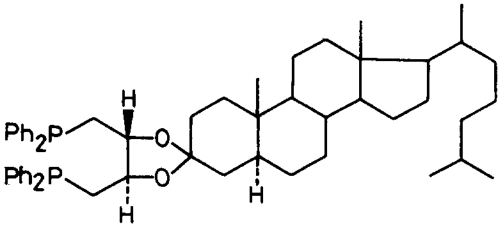


14

Complexes of Rh with the cationic, water-soluble phosphine $Ph_2PCH_2CH_2NMe_3^+,NO_3^-$ (L) catalyze the hydrogenation and hydroformylation of water-soluble and water-insoluble olefins. In the hydroformylation of 1-hexene, n:i aldehyde ratios of about 4:1 were obtained. Rhodium remained essentially in the water phase and could be easily separated from the organic products. Adsorption of $(NBD)RhL_3^{3+}$ onto the Na form of a strong acid ion-exchange resin resulted in a supported catalyst for the same reaction. Virtually no leaching of Rh was observed, although the Rh can easily be recovered by elution with acid [36]. $Rh_2(\mu\text{-}tBu_2P)_2(CO)_4$ catalyzes the hydroformylation of 1-hexene at room temperature and 2 bar. The catalyst remains active at elevated temperatures but under such conditions new phosphido-bridged species are formed [37]. Dinuclear thiolato-bridged Rh complexes, particularly $Rh_2(SBu^t)_2(CO)_2[P(OMe)_3]_2$ catalyze the hydroformylation of 1-hexene at 80°C and 5 bar (H_2:CO = 1:1). The complex remains unchanged under the reaction conditions. Dinuclear species are proposed as reaction intermediates [38].

The catalytic activity of $RhCl_3$ and $HRhCO(PPh_3)_3$ towards hydroformylation of olefins is enhanced by UV-irradiation. In the presence of NBD, $RhCl_3$ yields a catalyst which is active even at room temperature. The NBD is necessary only in catalytic amounts and remains unchanged until most of the olefin is converted [39].

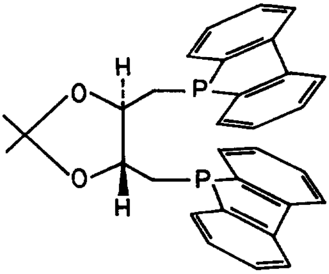
See also [13,14,15].

c) Pt catalysts

The complex systems formed from *cis*-$Pt(L)(PR_3)Cl_2$ + $SnCl_2.2H_2O$ (L = SMe_2, $ArNH_2$; R = aryl) catalyze the hydrogenation of olefins. These systems are more active than the corresponding ones obtained from cis-PtL_2Cl_2 or cis-$Pt(PR_3)_2Cl_2$ in the presence of $SnCl_2$. The complexes from cis-$Pt(CO)(PPh_3)Cl_2$ and $SnCl_2.2H_2O$ are active hydroformylation catalysts. NMR studies show that in these latter reaction mixtures the following complexes are present in acetone solution: cis-$Pt(CO)(PPh_3)Cl_2$, trans-$[Pt(CO)(PPh_3)_2Cl]^+$, $[Pt(SnCl_3)_5]^-$, trans-$[Pt(CO)(SnCl_3)_2Cl]^-$, and trans-$[Pt(PPh_3)(SnCl_3)_2Cl]^-$. The presence of all of these complexes seems to be necessary for catalytic activity [40]. The ligand rearrangement processes leading to these complexes have been investigated in detail using spectroscopic methods [41]. The reactions are strongly influenced by the solvent [42] and accordingly the catalytic activity of these systems is solvent dependent too: significantly higher turnover numbers were obtained in acetone than in dichloromethane [40].

The system $Pt(PPh_3)_2Cl_2$ + $SnCl_2$ catalyzes the hydroformylation of olefins in EtOH as solvent at 100°C and 130 bar ($CO:H_2$ = 1:1). Hydrocarboalkoxylation does not occur even in the presence of potential activating agents like HCl or LiCl [43].

Asymmetric hydroformylation of styrene with the chiral (-)-DIPHOL (15) + $PtCl_2$ + $SnCl_2$ catalyst system yields (+)-2-phenylpropanal with 73-80% o.y. [44]. These values are somewhat lower than those reported earlier for this reaction (Annual Survey 1982, ref.35).



15, (-)- DIPHOL

The selectivity of polymer-bound catalysts vs. their homogeneous counterparts was examined in the $Ru(CO)_3(PPh_3)_2$-catalyzed hydroformylation of 1-pentene and the [(-)-DIOP]$PtCl_2$ + $SnCl_2$-catalyzed hydroformylation of styrene [45].

See also [20].

d) Other Metals

Pente-1-ene-5-d_3 was hydrofomylated in the presence of $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$. Deuterium retention and redistribution differs with the two catalysts. Mainly the straight chain aldehyde isomer is formed [46].

The Os complex $HOs(CO)(PPh_3)_3Br$ has been found to be an efficient catalyst for C=C bond migration, hydrogenation of olefins, aldehydes, ketones and for hydroformylation of hexene-1. Reaction conditions are usually 150°C and 5-100 bar. Under conditions of hydroformylation the complex is transformed into $H_2Os(CO)_2(PPh_3)_2$ [47].

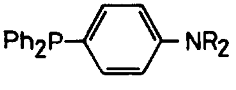
See also [45]

e) Heterogeneous Systems (Supported Complexes)

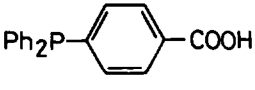
Polymer-anchored Co carbonyl phosphine complexes have been synthesized for use as hydroformylation catalysts. The chelated species Ⓟ—$C_6H_4P(Ph)CH_2CH_2PPh_2Co(CO)_3Co(CO)_3$ displayed a higher selectivity to n-hexanal when compared with the corresponding homogeneous catalytic species [48]. Polymerizable complexes of the type $RCCo_3(CO)_9$ which contain olefinic double bonds in the group R were prepared in order to evaluate their polymers as hydroformylation catalysts. Partial decomposition of the clusters occured under the reaction conditions (100°C and 70 bar CO + H_2) and the mononuclear species formed appear to be the actual catalysts [49]. A styrene-divinylbenzene polymer carrying $-C(O)CCo_3(CO)_9$ cluster groups has been prepared and used as a catalyst for hydroformylation of 1-heptene. Aldehyde selectivity was about 100% and no olefin hydrogenation was observed. The catalyst could be reused several times but gradually cobalt was lost from the polymer [50]. The cluster $Co_4(CO)_{10}(PPh)_2$ was heterogenized by bonding to polystyrene and used as catalyst for the hydroformylation of 1-hexene. The polymer-supported cluster was about 2 times as active than the same complex in solution. However, the thermal stability of the supported cluster is smaller [51].

Silica-supported $(RPPh_2)_2RhCo_3(CO)_{10}$ (R = silica) catalyzed 1-hexene hydroformylation at 100°C and 50 bar (CO + H_2) with about the same activity and selectivity as the non-supported Rh-Co cluster [52].

The basic and acidic functionalized phosphines (16) and (17) were attached to acidic and basic ion-exchange resins (Amberlyst type) and treated with $Rh_2(CO)_4Cl_2$ to obtain immobilized Rh-phosphine hydroformylation catalysts. The complexes supported on macroreticular ion-exchange resins provided high reaction rates for the hydroformylation of octene-1. Acidic or basic functionality of the phosphine ligand exerted little influence on the selectivity of the reaction [53].



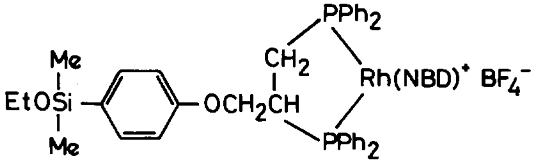
16 (R=Me,Et)



17

Pentene-1 was hydroformylated in the presence of Rh complexes supported on polyquinolines containing diphenylphosphinophenanthrene units [54].

Hydroformylation catalysts were prepared by treatment of silica gel with the Rh complex (18) and subsequently with $Me_3SiNHSiMe_3$. Turnover numbers were found to increase with increasing coverage of the surface with Rh complexes. This suggests that formation of aldehyde from the intermediate acylrhodium complex is a dinuclear elimination step which requires adjacent rhodium hydride and rhodium acyl. Isolated rhodium centers are inactive [55].



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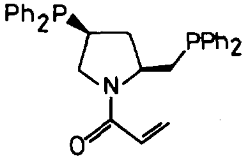
Cationic phosphinerhodium complex containing PPh_3 or the phosphinophosphonium ligand $Ph_2P(CH_2)_2PPh_2(CH_2Ph)^+$ intercalate into the swelling layered silicate hectorite by replacement of Na^+. These Rh complexes may be used as hydroformylation catalysts when acetone is the solvating medium. The PPh_3-containing complexes desorb rather easily under the reaction conditions but with the phosphonium ligand most of the hydroformylation reaction proceeds within the clay interlayers [56].

Polymers containing an optically active chelating phosphine ligand were obtained by copolymerizing (19) with hydroxyethyl methacrylate/ethylene dimethacrylate or with styrene/divinylbenzene. Platinum chloride was exchanged onto the polymer and hydroformylation of styrene was carried out in the presence of $SnCl_2$. Hydratropaldehyde was obtained with optical yields of 70-73% which are the highest values yet realized with a polymer-supported catalyst [57].



19

f) Modified Hydroformylations

The hydroformylation of formaldehyde

$$CH_2O + CO + H_2 \longrightarrow HOCH_2CHO$$

is catalyzed by Rh phosphine complexes in the presence of amines as bases at 110°C and 160 bar. For the best compromise of catalyst stability, activity and product selectivity, the PPh_3:Rh:Et_3N mol ratio has been found to be around 30:1:(3-4). The anionic complex $Rh(CO)_3PPh_3^-$ is regarded to be the active catalyst which attacks the formaldehyde as a nucleophile and Et_3NH^+ is the proton source which is necessary for the formation of the hydroxymethyl-rhodium species [58]:

$$CH_2O + Rh(CO)_3PPh_3^- + Et_3NH^+ \longrightarrow HOCH_2Rh(CO)_3PPh_3 + Et_3N$$

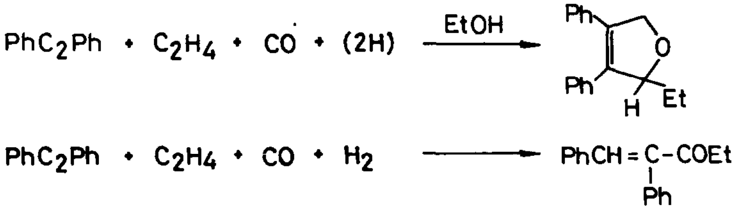
The hydrocarbonylation of acrylic acid derivatives with CO in iPrOH is catalyzed by $Rh_4(CO)_{12}$ at 180°C and 75 bar:

$$2\ CH_2{=}CHCOY + CO + Me_2CHOH \longrightarrow \underset{20}{OC(CH_2CH_2COY)_2} + Me_2CO$$

$Y = OMe, OEt, OBu, OCH_2CH(Et)Bu, NMe_2$

In addition to the γ-ketopimelic acid derivatives (20) propionic acid derivatives were formed as byproducts [59].

Using $Rh_4(CO)_{12}$ as catalyst, the cross-hydrocarbonylation of acetylene and ethylene with CO gives 5-ethyl-2(5H)-furanones (21) in hydrogen-donating solvents and α, β-unsaturated ethyl ketones if H_2 is introduced into the reacting system [60]:



21

See also [93].

3. Homologation of Alcohols and Esters with CO + H_2

The kinetics of the homologation of methanol to ethanol

$$CH_3OH + CO + 2H_2 \longrightarrow C_2H_5OH + H_2O$$

with $Co_2(CO)_8$ + I_2 as catalyst was investigated in the presence of PBu_3. The rate is first order in methanol, cobalt and CO. Hydrogen partial pressure does not affect the rate of methanol conversion [61]. The cobalt-catalyzed homologation of MeOH was investigated using CD_3OD. GC/MS measurements showed that the CD_3 group remains intact during the reaction. In the presence of iodine promoters MeI is formed under the reaction conditions. Experiments with CD_3I and CH_3OH did show, that methyl iodide is much more reactive than methanol. These results prove that MeI is an important intermediate in iodine-promoted methanol homologation [62].

Several multicomponent catalysts containing Co, Ru, PPh_3 and iodine were also tested for this reaction. Good results were achieved with the $CpRu(PPh_3)_2Cl$ + $Co_2(CO)_8$ + MeI system at 220°C and 270 bar (H_2:CO = 3:2). At very short reaction times the major product was acetaldehyde which was successively transformed into ethanol. Under such conditions the selectivity for ethanol was 80% [63]. Among the mixed-metal clusters containing Co as catalysts best results were obtained with different $M[RuCo_3(CO)_{12}]$ salts (where M = H, Na, Et_4N, Ph_4N or $(Ph_3P)_2N$). These catalysts were effective under relatively mild conditions (180-210°C, initial pressure 120 bar at room temperature). The selectivity of ethanol was 64% at a MeI promoter/ /cluster molar ratio of 9 [64,65].

The homologation of methanol with CO + H_2 to acetaldehyde

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

(which is successively transformed into its dimethyl acetal) in the presence of $Co(OAc)_2.4H_2O$ promoted by iodine was examined under various conditions. High pressures (1400 bar) and low temperatures (160-170°C) give best yields and selectivity to acetaldehyde [66]. Transition metal halides $MCl_3.3H_2O$ (M = Rh, Ir, Ru) promote the reaction. This effect has been investigated and found to be due to the formation of HI in the presence of LiI and CO. The observed rate enhancement is therefore not the result of metal cooperativity [67].

Methanol can be homologated to ethanol by CO + H_2O with Co-containing catalysts under basic conditions. Ethanol selectivity is about 60%, MeOAc and EtOAc are the main byproducts [68].

The homologation of MeOAc to EtOAc

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

was examined using the following catalysts: Ru, Co, Rh, Co + + Ru(Ni,Fe,Pd,Pt), Rh + Ru(Co). The most effective system was a combination of Co and Ru (Co/Ru = 1/2.5) at 200°C and 280 bar (CO/H_2 = 1/2) [69]. Methanol, ethanol and the carboxylic acid are formed as byproducts. With Co alone, acetaldehyde becomes the main product whereas Ru alone has only slight activity [70]. These binary homogeneous catalysts composed of Ru and Co were tested also for the reductive carbonylation of dimethyl ether by CO and H_2. In this case Co has no effect [71].

4. Coordination Chemistry Related to CO Hydrogenation and Hydroformylation

$[(\eta^5\text{-}C_5Me_4Et)TaCl_2H]_2$ reacts with CO to give $Ta_2(\eta^5\text{-}C_5Me_4Et)_2Cl_4(H)(CHO)$, the formyl in this complex bridges the two metals. Treating this formyl complex with $AlCl_3$ methane is formed, if hydrolyzed with aqueous HCl, MeOH is obtained [72]. Prolonged carbonylation of oligomeric zirconocene $[Cp_2ZrH_2]_x$ at room temperature yields the trimeric (η^2-formaldehyde)zirconocene complex $[Cp_2Zr(CH_2O)]_3$. This is the first example for the formation of a η^2-formaldehyde transition-metal complex from a metal hydride and CO [73].

The catalytic reduction of CO has been now successfully modelled with CO coordinated to iron, the metal operating as a catalyst in the Fischer-Tropsch process. Reduction of $(C_5Me_5)Fe(CO)_3^+$ with $NaBH_4$ leads to the corresponding hydride, hydroxymethyl or methyl complexes $(C_5Me_5)Fe(CO)_2R$ (R = H, CH_2OH, Me) with excellent yields (80-100%). The structure of the main product is determined by the solvent used [74]. After an induction period solutions of $HFe_4(CH)(CO)_{12}$ in HSO_3CF_3 slowly produce methane at room temperature. Experiments suggest that the reducing equivalents for the conversion of CH to methane are furnished by reducing species "$Fe_x(CO)_y$" which are formed as byproducts [75]. $HRu(CO)_4^-$ converts $CpRe(CO)_2(NO)^+$ into the formyl complex CpRe(CO)(NO)(CHO). This reaction demonstrates that H can be transferred from a transition metal hydride to an electrophilic carbonyl ligand which may be a feasible step in the homogeneous CO reduction process catalyzed by metal carbonyls [76].

The stoichiometric hydrogenation and hydroformylation of some cyclopropenes and 1,1-diphenyl ethylene with $HMn(CO)_5$ has been investigated in detergent solutions. A substantial increase in the yield of aldehydes at the expense of the hydrogenated products has been observed. This is in accordance with the mechanism proposed earlier which implies the intermediacy of caged geminate radical pairs because the escape of these from the cage should be retarted by micelle sequestering [77].

The reaction of H_2 with $Co_2(CO)_8$ to form $HCo(CO)_4$ is the only step of the hydroformylation catalytic cycle which needs high pressures and temperatures. This reaction is catalyzed by bases like tertiary amines, N heterocycles, tertiary phosphines and halide ions. The $Co_2(CO)_8$ conversion generally shows a maximum with increasing base concentration [78]. The reaction of $HCo(CO)_4$ with aliphatic olefins and CO to form acylcobalt tetracarbonyl complexes and aldehydes, and the stoichiometric hydrogenation of aliphatic olefins with $HCo(CO)_4$ require the presence of $Co_2(CO)_8$. The ratio of carbonylation to hydrogenation decreases in the order 1-heptene >2- or 3-heptene > ethyl acrylate. Higher temperatures favor hydrogenation over carbonylation [79]. The hydrogenolysis of acylcobalt tetracarbonyls to aldehydes is an important step of the hydroformylation catalytic cycle. This step has now been modelled by investigating the reaction between $EtOOCCo(CO)_4$ and H_2 or $HCo(CO)_4$. It was found that the reaction with $HCo(CO)_4$ was 12 times as fast as that with H_2 [80].

An X-ray molecular structure analysis of Ir(COD)[(-)-DIPHOL]Cl was carried out [(-)-DIPHOL = 15]. Although (-)-DIPHOL has the same chiral backbone as (-)-DIOP (11) the steric environment around the π-olefin coordination site on the metal in the analogous DIPHOL and DIOP complexes is greatly changed. This explains why the prevailing absolute configurations of aldehydes obtained by hydroformylation of olefins with DIPHOL or DIOP-containing Rh complex are opposite [81].

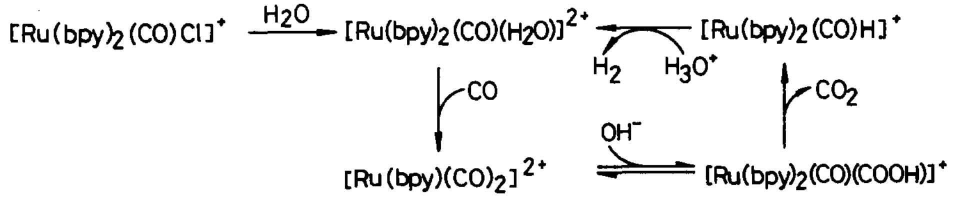
The $HFe_3(CO)_{11}^-$ anion reacts with ethylene at room temperature to give $Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)^-$. This trinuclear anion is transformed by CO into the mononuclear $Fe(CO)_4(COC_2H_5)^-$ which is a further proof that the $HFe_3(CO)_{11}^-$ anion is not the real catalyst in the Reppe-synthesis of alcohols. With H_2 extensive decomposition occurs and ethane, propanal and propanol can be detected in the product [82].

It was shown that hydrogenation of $MeCOCo(CO)_3PMePh_2$ with H_2 yields acetaldehyde, ethanol and ethyl formate. Since the same compounds are formed during the homologation of methanol this result supports the suggestion that acetylcobalt carbonyls are intermediates of this reaction [83].

5. Water Gas Shift Reaction

The $HFe_3(CO)_{11}^-$/NaY system prepared by adsorption of $Fe_2(CO)_9$ on NaY zeolite is an active catalyst for the water gas shift reaction in the range 60-180°C [84].

The water gas shift reaction is catalyzed by $Ru(bpy)(CO)Cl^+$ in aqueous alkaline medium at 150°C and 5 bar CO pressure. Based on kinetic and spectroscopic measurements the following mechanism has been proposed [85]:



The water soluble Ru(II) porphyrin $Ru(TPPS)(CO)^{4-}$ [TPPS = meso-tetra(4-sulfonatophenyl)porphyrinato] also catalyzes the water gas shift reaction in a basic water solution. This Ru complex is significantly more active than $Ru_3(CO)_{12}$ [86].

Homogeneous catalysis of the water gas shift reaction has been demonstrated for a system based upon $Ru_3(CO)_{12}$ in aqueous acidic diglyme solutions. In situ spectroscopic studies on the working catalyst lead to the formulation of $[HRu_2(CO)_{9-x}(OR)_x]^+$ as the principal species. At higher CO pressures the catalyst system is deactivated due to the formation of $Ru_3(CO)_{12}$ and $Ru(CO)_5$ [87]. If 1,8-diazabicyclo[3,4,0]undecene-7 is used as the basic cocatalyst for the water gas shift reaction catalyzed by $M_3(CO)_{12}$ (M = Ru, Os) efficient catalysts are formed even from $Os_3(CO)_{12}$. The dianion clusters $H_2M_4(CO)_{12}^{2-}$ were isolated from these reaction mixtures [88]. The hydrogenation of ethylene at 70-100°C catalyzed by the surface graft compound $HOs_3(CO)_{10}$-SiO_2 and the water gas shift reaction at 20-120°C with $Rh_6(CO)_{16}$ adsorbed on Al_2O_3 was studied. Mechanisms were proposed for both catalytic reactions [89].

Amine complexes of Ir supported on a 13-X faujasite type zeolite catalyze the water gas shift reaction at 140-220°C. Carbonyl complexes are formed during the reaction and can be detected spectroscopically [90].

Transition metal carbonates catalyze the water gas shift reaction in a pressurized aqueous system (water as a liquid phase) at 300°C. Among the metals tested Ni carbonate was the most active. Methane was formed as byproduct [91].

See also [92]

6. Reduction with CO + H_2O

The C=C double bond of benzalacetone is hydrogenated by CO+H_2O with $Rh_6(CO)_{16}$, $Ir_4(CO)_{12}$, $Rh(PPh_3)_3Cl$ or $Rh(diene)P_2$ complexes as catalysts (P_2 = bidentate phosphine or two monodentate phosphines). The rate of reaction is increased by ethylenediamine and if ethanol is present. The latter complexes also catalyze the water gas shift reaction which is fastest at pH = 2 [92]. Several Rh(I) hydrides with trialkylphosphine ligands [e.g. $HRh(N_2)(PBu^t_3)_2$ and $H_2Rh_2(\mu\text{-}N_2)(PCy_3)_4$] were prepared by reducing $RhCl_3.3H_2O$ with Na amalgam in THF. These complexes serve as efficient catalysts for the hydrogenation of nitriles, ketones and alkynes, the hydrogenation of carbonyl and nitro compounds with CO + H_2O and olefin hydroformylation with CH_2O [93].

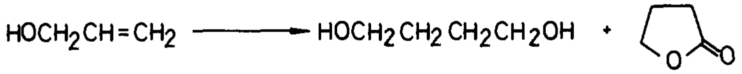
N-benzylideneaniline is reduced to N-benzylaniline by CO+ H_2O in the presence of $Fe(CO)_5$ and a base at 100°C and 100 bar. The

$HFe(CO)_4^-$ anion is regarded as the catalytically active species which acts as a hydride donor. Water serves as a proton source. If Et_3N is used as a base, transalkylations take place [94].

Nitrobenzene is reduced to aniline by $CO+H_2O$ if $Rh_6(CO)_{16}$ or $Ru_3(CO)_{12}$ are used as catalyst precursors and phen or 3,4,7,8-tetramethyl phen as nitrogen bases at 165°C and 30 bar [95]. Nitroarenes are reduced to aminoarenes with $CO+H_2O$ in the presence of $Pt(PPh_3)_2Cl_2 + SnCl_4 + Et_3N$ at 80°C and 60 bar. The catalyst system appears to be chemoselective since alpihatic nitro compounds, α,β-unsaturated carbonyl compounds and acetylenes did not react under these conditions [96].

7. Miscellaneous Reductive Transformations of CO and CO_2

The formation of 1,4-butadienol from allyl alcohol, CO and H_2O is catalyzed by $Rh_6(CO)_{16}$ in the presence of $Me_2NCH_2CH_2NMe_2$ at 60°C and 10 bar. The main side product is γ-butyrolacetone:



Et_3N or KOH are ineffective as bases under such conditions [97]. In a reaction closely related to hydroformylation organic halides may be converted with CO and tin hydrides into aldehydes. The reaction is catalyzed by $Pd(PPh_3)_4$ and requires mild conditions (50°C and 1-3 bar) [98]:

$$RX + CO + Bu_3SnH \longrightarrow RCHO + Bu_3SnX$$

It has been found that $HRu_3(CO)_{11}^-$ is an effective catalyst precursor for the production of methyl formate from CO_2 at 125°C and 30 bar:

$$CO_2 + H_2 + CH_3OH \longrightarrow HCOOCH_3 + H_2O$$

Probably the tetranuclear species $H_3Ru_4(CO)_{12}^-$ is the catalytically active one. The results suggest that the reaction is <u>not</u> preceeded by the water gas shift reaction [99].

III. Hydrogenation and Reduction

1. H-D Exchange

Addition of 1-dodecanol to a suspension of H_2CrO_4/SiO_2 plus $NaBD_4/Al_2O_3$ in ether at room temperature leads to the formation of 1-dodecanol 1,1-d_2. This H-D-exchange is made possible by repeated oxidations to carboxylic acid and reductions to alcohol [100].

H-D exchange between aromatic or α , β -unsaturated carboxylic acids and D_2O in the presence of $RhCl_3$ occurs with high selectivity at positions β to the COOH group [101]. The complex $H_3Ir(CO)(diphos)$ undergoes H-D exchange with benzene-d_6 under irradiation. If CO is present, small amounts of benzaldehyde are formed [102].

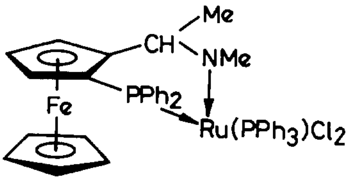
An LFER was found between the catalytic activity of $[Pt(H_2O)_nCl_{4-n}]_n^{2-}$ (n = 0-4) in the H-D exchange for alkanes and the distortion energies of these square planar complexes [103]. H-D exchange in aromatic and cycloaliphatic hydrocarbons and in thiophenes was studied in the presence of Pt(II) complexes. Multiple H-D exchange occured in benzene [104]. The deuteration of benzofuran and 3-methylbenzothiophene is catalyzed by K_2PtCl_4 [105].

2. Hydrogenation of Olefins

a) Fe, Ru and Os Catalysts

The cluster $Fe_4S_4Cl_4^{2-}$ catalyzes the hydrogenation of octenes in the presence of PhLi. The selectivity of the catalyst system depends on the solvent used, in HMPA only octene-1 is hydrogenated [106]. The hydrogenation catalysts obtained from $Fe(st)_3$ and $AlEt_3$ have been investigated by Mössbauer spectroscopy. Samples with Al:Fe = 5-11 had high catalytic activity [107].

A kinetic study of the hydrogenation of allyl alcohol and allyl bromide using $Ru(PPh_3)_3Cl_2$ as catalyst has been reported. The catalyst rapidly deactivates during allyl alcohol hydrogenation because of the formation of inactive $Ru(CO)(PPh_3)_2Cl_2$ [108]. The Ru complex (22) catalyzes the hydrogenation of terminal olefins under mild conditions. Kinetic measurements performed with hexene-1 in nBuOH suggest a mechanism according to which the active species is formed from (22) by absorption of 0.5 mol H_2 and dissociation of a PPh_3 ligand [109].



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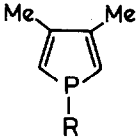
Ruthenium(II) complexes of 1-substituted 3,4-dimethylphospholes (L = 23) catalyze the hydrogenation of 1-heptene at atmospheric pressure and room temperature. Complexes of the type RuL_4Cl_2 and $RuL_2(PPh_3)Cl_2$ have been found to be of roughly equal activity [110].



23., R = Me, tBu

The water-soluble catalysts $Ru(tmp)_2Cl_2$ and $Rh(tmp)_3Cl$ have been succesfully applied for the hydrogenation of the unsaturated fatty acid content of liposomes and biomembranes. The Ru complex is more active at low (physiological) temperatures [111]. Near--ultraviolet irradiation of $H_4Ru_4(CO)_{12}$ in heptane solution induces the catalytic hydrogenation of ethylene at 35°C. The mechanism is analogous with that proposed for the same reaction under thermal conditions and involves $H_4Ru_4(CO)_{11}$ as an active intermediate [112].

The cluster $H_2RuOs_3(CO)_{13}$ adsorbed onto Al_2O_3 is transformed under H_2 + CO into the surface cluster $[H_3RuOs_3(CO)_{12}]^-$. This cluster was stable in H_2 + CO up to 200°C and catalytically active for ethylene hydrogenation at 70°C [113]. The cluster $CpNiOs_3(CO)_9H_3$ supported on γ-alumina is an efficient catalyst for the hydrogenation of olefins at room temperature and for the hydrogenation of CO or CO_2 to methane at temperatures above 250°C. This complex is thus the most active "cluster based" catalyst for the methanation of CO_2 [114].

See also [47,89]

b) Co, Rh and Ir Catalysts

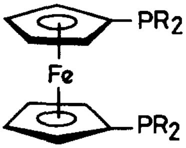
The mechanism of the splitting of H_2 by $Co(CN)_5^{3-}$ in aqueous solution has been a matter of dispute [115-117]. The experimental evidence supports homolytic splitting [117]:

$$H_2 + 2Co(CN)_5^{3-} \longrightarrow 2Co(CN)_5H^{3-}$$

The hydrogenation of the cinnamate ion in aqueous solution with the $Co(CN)_5H^{3-}$ ion as a catalyst has been reinvestigated. The rate law suggested earlier has been confirmed and the activation energy was determined as 14.5 ± 0.5 $kcal.mol^{-1}$ [118].

Diarylethylenes are hydrogenated on treatment with $Co_2(CO)_8$ or its bis-tributylphosphine substituted derivative dissolved in benzene, aqueous HBF_4, and sodium 4-dodecylbenzenesulfonate. This is the first example of organometallic phase transfer catalysis under acidic conditions. Presumably a cobalt carbonyl hydride, generated in situ, is the stoichiometric hydrogenating agent [119]. The selective hydrogenation of vegetable oils has been examined with $Co_2(CO)_8$, Ni-containing Ziegler-type catalysts and diphenylphosphinostyrene-divinylbenzene-supported $PdCl_2$. With all these catalysts hydrogenation could be performed on crude oils [120].

The kinetics of allyl alcohol hydrogenation with $Rh(PPh_3)_3Cl$ has been studied. At higher alcohol concentrations the reaction is inhibited by the substrate. With increasing reaction time the catalyst is gradually deactivated due to the formation of $Rh(CO)(PPh_3)_2Cl$ [121]. The thiophene analog of the Wilkinson complex, $Rh[P(2\text{-thienyl})_3]_3Cl$ was prepared and used as catalyst for the hydrogenation of olefins [122]. The cationic Rh complexes $[(PP)Rh(NBD)](ClO_4)$ containing the new bis tertiary phosphines PP = (24) or (25), have been used as catalysts for the hydrogenation of α,β-unsaturated carboxylic acids. For substrates demanding only one coordination site the tBu derivative (24) was found to be the more active but with (acylamino)acrylic and (acylamino)cinnamic acids which are chelating substrates the Ph derivative (25) formed the more active catalyst [123].



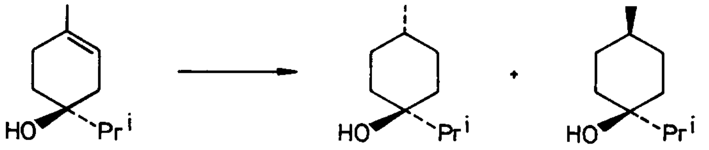
24, R = tBu
25, R = Ph

Intercalated clay catalysts, formed by interlayering of Na^+-hectorite with $Rh(NBD)(PPh_3)_2^+$ or $Rh(NBD)(dppe)^+$ were used as catalysts for the hydrogenation and isomerization of hexene-1 in MeOH. Surface acidity had a pronounced influence on the reaction in the case of the PPh_3-containing catalyst [124].

The diphenylphosphido-bridged Rh complexes $[Rh(PPh_2)(COD)]_2$, $(dppe)Rh(PPh_2)_2Rh(COD)$, and $(PPh_3)_2Rh(PPh_2)_2Rh(COD)$ catalyze the hydrogenation of olefins at ambient conditions. The activity of these catalysts is comparable to that of the Wilkinson catalyst, $Rh(PPh_3)_3Cl$. The bimetallic nature of the complexes is probably retained during hydrogenation [125]. The coordinatively unsaturated clusters $\{[(MeO)_2PCH_2CH_2P(OMe)]RhH\}_4$ and $\{[(iPrO)_2PCH_2CH_2P(OPr^i]_2\,RhH\}_2$ catalyze the hydrogenation of terminal and internal olefins [126].

The ion pair $[(C_8H_{17})_3NCH_3]^+[RhCl_4]^-$ formed from aqueous rhodium trichloride and methyltrioctylammonium chloride (Aliquat-336) in dichloroethane catalyzes the hydrogenation of olefins, acetylenes and aromatic compounds under mild conditions (30°C and 1 bar H_2). The reaction is preceeded by a long induction period. Acetylenes inhibit the hydrogenation of olefins and olefins inhibit the hydrogenation of aromatics. Both liquid phases remain homogeneous during the reaction [127].

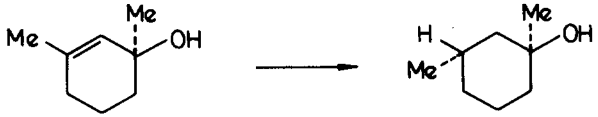
The hydrogenation of terpinen-4-ol (26) is catalyzed by $[(COD)Ir(PCy_3)(py)](PF_6)$ with a ca. 1000:1 preference for H_2 addition to the face of the substrate bearing the OH group:



26 99.9% 0.1%

This effect is due to chelation of the alcohol to the catalyst as evidenced by NMR spectroscopy [128]. Cyclohexanols with allylic or homoallylic double bonds like (27) or (28) are hydrogenated with high stereoselectivity with $[Ir(COD)(py)(PCy_3)](PF_6)$ as catalyst. The stereoselectivity increases in the order primary < secondary < tertiary alcohols from about 85% to over 99%. Practically no stereoselectivity is observed with heterogeneous catalysts [129].

27

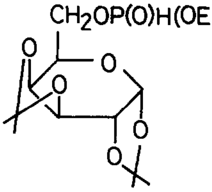


28

See also [111].

c) Ni, Pd and Pt catalysts

Palladium complexes of the type $Pd_2Cl_2L_4$ have been prepared with L = dialkyl phosphites $[P(O)H(OR)_2]$ and used as catalysts for the hydrogenation of olefins, acetylenes and nitrobenzene. Applying the chiral phosphites (29-31) obtained from sugars as ligands enantioselective catalysts were obtained which hydrogenated unsaturated carboxylic acids with optical yields up to 27% [130,131].



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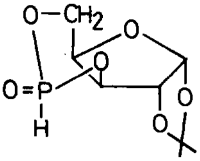

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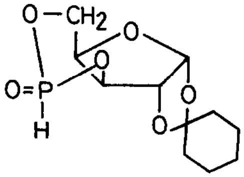


31

Alkenes may be hydrogenated with $[Pd_5(PPh)_2]_n$ and $[Pd_{10}(bpy)_4(O_2)_3](OAc)_2$ as catalysts. The hydrogenating activity is destroyed by sulfur compounds but can be restored by treating the poisoned catalyst with alkynes under H_2 [132].

Dimethylaminated polystyrene-anchored $PdCl_2$ complexes were used as catalysts for the hydrogenation of olefins at atmospheric pressure. The activity of the catalysts decreased with increasing N/Pd ratio [133]. Polymer-anchored Pd complexes, prepared from acrylonitrile-90% divinylbenzene copolymer or 2-N-vinylpyrrolidone--70% divinylbenzene copolymer and Pd(II) salts in aqueous dioxane, catalyze the hydrogenation of olefins at ambient pressure and temperature. The kinetics of the reaction were determined [134].

Diphenylphosphino moieties containing groups like $(CH_2)_3PPh_2$ were anchored to SiO_2. The Pd complexes of these polymeric phosphines catalyze the hydrogenation olefins, over 10^4 cycles per site were achieved [135]. The Pd complex of poly-4-oxa-7-diphenylphosphino-6--hydroxyheptylsiloxane supported on SiO_2 displays high activity for the hydrogenation of olefinic compounds containing aromatic, cyano, carboxy, and ester groups and being soluble in water. It can be reused several times [136].

The complexes $M(PR_3)_2Cl_2$ (M = Pd, Pt; R = long-chain n-alkyl or p-n-alkylphenyl) catalyze the hydrogenation of methyl linoleate and methyl linoleate selectively to monoenes in the presence of $SnCl_2$. Reaction conditions are 90°C and 40 bar. The efficiency of the catalysts strongly depends on the solvent: in benzene-methanol Pd complexes were more active than their Pt counterparts but partly decomposed during hydrogenation into an inactive black precipitate [137]. The Pt species were more active in the absence of solvent and under such conditions much less decomposition of Pd complexes occured [138]. The chloro-bridged complex $[PtCl_2(2,4,6\text{-}Me_3py)]_2$ catalyzes the hydrogenation and hydrosilylation of olefins at room temperature and atmospheric pressure. The new catalyst is stable in air and well soluble in most organic solvents [139].

See also [40, 41, 42, 171]

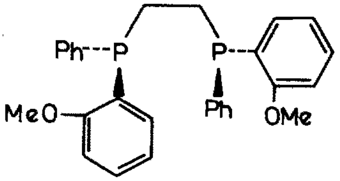
3. Asymmetric Hydrogenation of Olefins

Systems containing $AlEt_3$, $Co(acac)_2$ and Ph_2PR (R = neomenthyl, menthyloxy) catalyze the asymmetric hydrogenation of cis- and trans--MeCPh=CHMe and $PhC(OEt)=CH_2$ with low optical yields [140]. The hydrogenation of styrene was studied with several Co-phosphine complexes as catalysts: $H_3Co(PPh_3)_3$, $H(N_2)Co(PPh_3)_3$ and $(N_2)Co(PPh_3)_3$. The catalytic systems $Co(acac)_2$ + $P(nmen)Ph_2$[or $P(Omen)Ph_2$] + $AlEt_3$ were used for the asymmetric hydrogenation of 2-phenylbutenes and α-ethoxystyrene [141]. The hydrogenation of the C=C double bond of prochiral α,β-unsaturated ketones (e.g.32) with $Co_2(CO)_6[(nmen)PPh_2]_2$ as catalyst at 100°C and 30 bar gave ketones with optical yields 1.4-16% [142].

32

2-Phenylbutene-1 is hydrogenated in the presence of $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ to give 2-phenylbutane with a maximum optical purity of 8.5%. This low optical yield is due (among other factors) to the isomerization of the substrate taking place during hydrogenation [143].

Earlier studies of the $[(dppe)Rh]^+$-catalyzed hydrogenation of (Z)-α-acetamidocinnamic acid methyl ester and hexene-1 have been extended to similar catalysts containing larger chelating diphosphine ligands, i.e. $Ph_2P(CH_2)_nPPh_2$ (n = 3,4 and 5) and DIOP. Equilibrium constants for the binding of the olefinic substrates to the catalyst and catalytic hydrogenation rates have been compared [144]. <u>para</u>-Enriched H_2 is converted into the <u>ortho</u>-<u>para</u> equilibrium mixture during hydrogenation of cyclohexene with $Rh(PPh_3)_3Cl$ as catalyst showing that the addition of H_2 to Rh is reversible. No equilibration occurs, however, during the course of hydrogenation of (Z)-α-benzamidocinnamic acid by cationic chelate Rh complexes with ditertiary phosphines like DIPAMP (33), thus demonstrating that addition of H_2 to Rh is irreversible in this case [145].

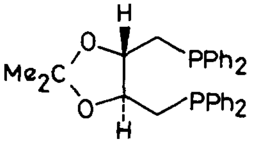


33, (-)-DIPAMP

Asymmetric hydrogenation of dehydro amino acids with chiral Rh-diphosphine complexes involves enamide complexes as intermediates containing the enamide as a bidentate chelating ligand. It has been shown now that the interconversion of these diastereoisomeric complexes occurs by an intramolecular mechanism over a complex containing the enamide as a monodentate ligand coordinated to Rh only with its carbonyl O atom [146].

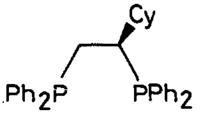
Six different dehydroaminoacids were enantioselectively hydrogenated using catalysts obtained <u>in situ</u> from $Rh_2(NBD)_2Cl_2$ and chiral diphosphines. The analysis of the results with the Ruch/Ugi theory showed that, even knowing the λ-parameters of the substrate substituents and the ϱ-parameters of the catalysts, the enantioselectivities calculated differed strongly from those obtained experimentally [147]. A correlation between the highest optical yields achieved in the asymmetric hydrogenation of α-acetamidocinnamic acid and the structure of the complexes formed between Rh and the chiral bis(diphenylphosphino) ligands has been proposed [148].

N-acetyl and N-benzoyl dehydrotryptophan was enantioselectively hydrogenated with Rh(I) complexes as catalysts in the presence of (+) and (-)-DIOP [(33a) and (11)] as chiral ligands. Highest o.y. was 86% [149].



33a, (+)-DIOP

The relative rates of hydrogenation of various substrates and the optical yields obtained with the Rh(I) complex of (R)-Cycphos (34) were reported and compared to the results obtained with analogous catalysts. These studied revealed that this ligand affords not only high optical yields but also relatively fast chemical rates. This is interpreted as the result of the high degree of flexibility in the ligand [150].



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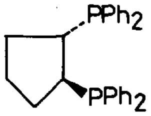

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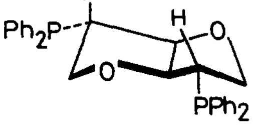
The (-)-(S,S) enantiomer of trans-1,2-bis(diphenylphosphino) cyclopentane (35) was prepared starting from cyclopentene and was used as a chiral ligand for asymmetric hydrogenation with $Rh_2(COD)_2Cl_2$ as catalyst precursor. The optical purity of the products obtained from N-benzamido cinnamic acid and its methyl ester were found to be 100±2% [151]. The chiral 1,4-diphosphine (36) has been prepared from D-mannitol. Rhodium complexes of this ligand are asymmetric homogeneous hydrogenation catalysts for dehydroamino acids, giving (S)-amino acids in up to 58% optical yields [152].



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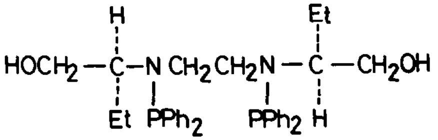
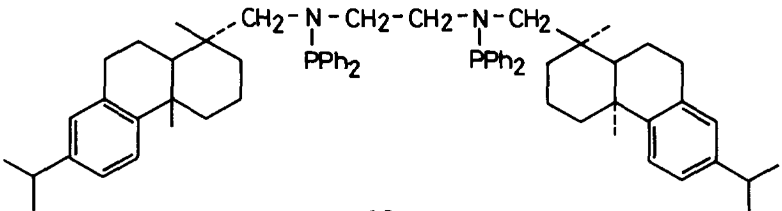


$HOCH_2-\overset{H}{\underset{Et}{C}}-\underset{PPh_2}{N}CH_2CH_2\underset{PPh_2}{N}-\overset{Et}{\underset{H}{C}}-CH_2OH$

37

Several new chiral aminophosphines have been prepared (37,38 and the atropisomeric 39) and used as ligands in asymmetric hydrogenation of dehydro amino acids with Rh(I) complexes as catalysts [153,154,155]. By using the two new chiral aminophosphine-phosphinite ligands (S)-Prolophos (40) and (S)-Butaphos (41) as ligands, (S)-aminoacids were obtained in 23-96% optical yields in asymmetric hydrogenation of dehydro amino acids with Rh complexes as catalysts [156].



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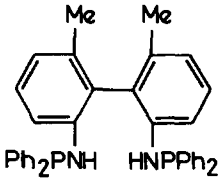
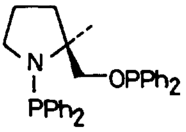


39, MABP



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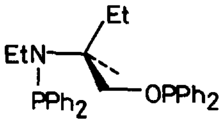
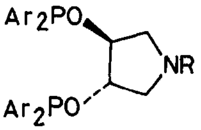


41

The new chiral diphosphinites (42-46) have been used as ligands for the asymmetric hydrogenation of dehydrodipeptides. The diphosphinites containing terminal amino groups (43,44 and 46) were very effective in the case of dehydropeptides containing a free carboxyl group, e.g. Ac-ΔPhe-(S)-Ala-OH. This suggests that also the electrostatic interaction between the ligand and the substrate is important for the discrimination of the prochiral face [157].

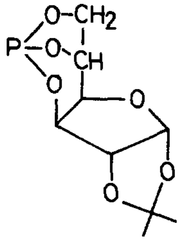


	R	Ar
42	$CH_2CH_2CHMe_2$	Ph
43	$CH_2CH_2NMe_2$	Ph
44	$CH_2CH_2CH_2NMe_2$	Ph
45	$CH_2CH_2CHMe_2$	p-anisyl
46	$CH_2CH_2NMe_2$	p-anisyl

The cluster $Rh_6(CO)_{10}[(-)DIOP]_3$ has been prepared from $Rh_6(CO)_{16}$ and (-)-DIOP and used as catalyst for the asymmetric hydrogenation of α-aminocinnamic acid derivatives. Rates were low and enantiomeric excess of the (R) isomers did not exceed 47% [158].

Enantioselective hydrogenation of α-acetamido cinnamic acid with $Rh(PPh_3)_3Cl$ catalyst was carried out in a cholesteryl tridecanoate crystal. The optical yield of the (-)-enantiomer reached a maximum (16%) in the mesophase temperature interval [159, 160].

The Pd and Rh complexes (η^3-C_3H_5)PdLCl and $Rh(CO)L_2Cl$ (L = 47) were used as catalysts for the hydrogenation of 1-decene and methylenesuccinic acid [161]. Tetrasubstituted amido-alkenes of type (47a) have been hydrogenated under mild conditions using $[Ir(COD)(NCPh)(L)]ClO_4$ complexes as catalysts (L = PCy_3 or P(nmen)Ph_2). Highest optical yield obtained with the chiral phosphine was 27% [162].



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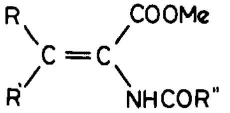


47a

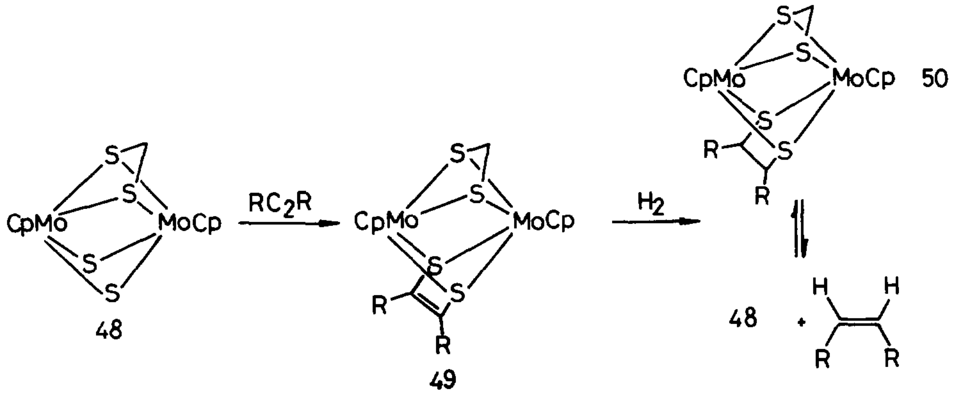
R, R', R" = Me or Ph

See also [32,35]

4. Hydrogenation of Dienes and Alkynes

a) Cr, Mo and W Catalysts

The hydrogenation of α-terpinene and 2,3-dihydroanisole is catalyzed by (phenanthrene)$Cr(CO)_3$ at 80° and 10 bar. The catalytic reaction is significantly accelerated by adding ketones to the reaction mixture. No asymmetric induction is observed in the presence of chiral ketones, however [163]. The complexes $Cp_2Mo_2(CO)_4(\mu\text{-}RCC(H)R)(CF_3COO)$ formed from $Cp_2Mo_2(CO)_4$, acetylenes (RCCR) and CF_3COOH are hydrogenated to alkenes at 2 bar and 30°C. These complexes can not be used, however, to catalyze the hydrogenation of acetylenes because, in the presence of excess acetylene, polymerization is the main reaction [164]. The stoichiometric hydrogenation of alkynes to cis-alkenes has been realized over complexes (48-50). Despite regeneration of (48) the reactions could not be closed to a catalytic cycle [165].



A vinylpyridine copolymer coordinated Mo-Fe-S cluster catalyst was prepared and used for acetylene hydrogenation [166]. Vinyl molybdate species were detected as reactive intermediates in the molybdothiol-catalyzed reduction of acetylene to ethylene by $NaBH_4$ or $[Fe_4S_4(SPr)_4]^{n-}$ (n = 2,3,4) [167].

b) Co, Rh and Ir Catalysts

The dinuclear hydride $(HRh[P(OPr^i)_3]_2)_2$ is a catalyst precursor for stereoselective hydrogenation of dialkyl- and diarylalkynes to the corresonding trans-alkenes. The rate-determining step in the catalytic cycle appears to be H addition to a dinuclear bridged vinyl derivative. In a competitive reaction this vinyl complex is transformed to a mononuclear species which is the catalyst precursor for the formation of cis-alkenes. As a result of this, the stereoselectivity of the original catalyst precursor for the formation of trans-alkenes rapidly diminishes with reaction time. These observations underscore the oft-described flaw in cluster catalysis, namely, generation of mononuclear species [168]. The cyclooctadiene isomers 1,3- and 1,5-COD are selectively hydrogenated to cyclooctene in the presence of Rh(1,5-COD)(1,3,5-cyclooctatriene) as catalyst. The isomerisation to 1,3-COD seems to be a necessary step for the hydrogenation of 1,5-COD, in accordance with this NBD in not hydrogenated [169]. The hydrogenation of acetylene and methyl acetylene with a supported $Rh(PPh_3)_3Cl$ catalyst was studied in a fixed-bed reactor at 1 bar and 60-90°C. Excess PPh_3 was essential for catalyst activity. The catalyst was 100% selective for olefin formation but in the case of acetylene it suffered progressive deactivation. Best catalyst activity was achieved with a macroporous silicagel support and a weakly coordinating solvent [170].

c) Ni, Pd and Pt Catalysts

Systems prepared *in situ* from $[Pd(OAc)_2]_3 + 3\ PR_3$ catalyze the hydrogenation of 3-heptyne to *cis*-3-heptene. The rate of alkyne reduction showed a strong dependence on the structure of the phosphine ligand while the product distribution changed only slightly. After all alkyne has been consumed the olefin was slowly isomerized and reduced to alkane [171].

The heteronuclear Pt clusters $Pt_2Co_2(CO)_8(PPh_3)_2$ and $Pt(CNC_6H_{11})_2[CpMo(CO)_3]_2$ catalyze the hydrogenation of terminal acetylenes. The Pt-Mo cluster can be recovered unchanged from the reaction mixture but the Pt-Co cluster undergoes complex molecular rearrangements [172]. The complexes of the type $(\pi\text{-allyl})Pt(PBu^t_3)H$ catalyze the hydrogenation of conjugated dienes to monoolefins at temperatures below -30°C. The selectivity for monoenes is practically 100%, the rate of the reaction decreases with increasing temperature [173].

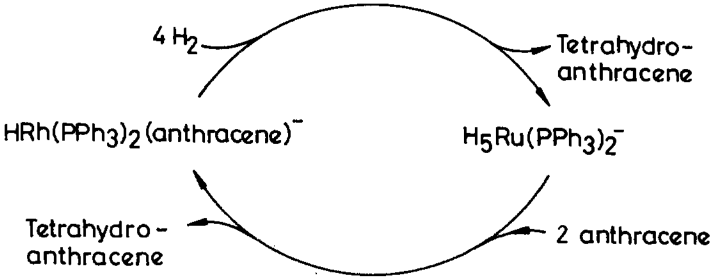
d) Other Metals

Diphenyl acetylene can be hydrogenated to stilbene (cis/trans ratio 95/5) with 1 bar H_2 in THF using $Cp_2V_2(CO)_5$ as catalyst precursor and irradiating the reaction mixture. Thermal hydrogenation is negligible. At large (100:1) substrate: catalyst ratios the hydrogenation is inhibited due to the formation of mononuclear acetylene complexes which are inactive [174].

Acetylene is reduced with 98% selectivity to ethylene by a $CuSO_4 + KBH_4 + H_2O$ catalyst system. H addition is *cis* [175].

5. Hydrogenation of Arenes and Heterocyclic Compounds

The reactions of several hydrido(phosphine)ruthenate complexes with H_2 and anthracene have been investigated. Based on the results the following catalytic cycle for the homogeneous hydrogenation of anthracene has been proposed [176]:



Kinetic data for benzene hydrogenation in the presence of $(\eta^3\text{-}C_3H_5)Co[P(OPr^i)_3]_3$ and the D isotope effect observed indicate that the rate-determining step is the addition of H_2 to a benzene-catalyst complex [177].

Hydrogenation of anthracenes, substituted anthracenes, and naphtalene is catalyzed by the corresponding $Rh(dppe)(arene)^+$ complexes at 60°C and atmospheric pressure. The kinetics of the reaction has been studied with 9-CF_3CO-anthracene in detail. The suggested stepwise mechanism involves the formation of 1,2-dihydro-anthracene as the first product over a σ -alkyl rhodium hydride intermediate in a way which is analogous to that demonstrated for the hydrogenation of olefins with a similar Rh-dppe catalyst [178]. Hydrogenation of aromatic hydrocarbons and of pyridine is catalyzed by $Rh(acac)[P(OPh)_3]_2$ at 80°C and 10 bar H_2. The catalyst is not sensitive to air but excess triphenyl phosphite decreases its activity [179]. Complexes prepared from $RhCl_3.xH_2O$ and N-phenyl-anthranilic acid catalyze the hydrogenation of aromatic and hetero-aromatic compounds. Only low and irreproducible reaction rates were obtained with aromatic hydrocarbons, but pyridine or quinoline are hydrogenated much more readily [180].

Arenes and heterocyclic compounds are hydrogenated at room temperature and 1 bar with $Rh_2(HD)_2Cl_2$ as catalyst in a two-phase system (hexane/water) in the presence of a quaternary ammonium salt as phase-transfer catalyst. The pH is critical and has to be regulated between 7.4 and 7.6 with a suitable buffer. Electron-donating substituents activate the arene ring toward hydrogenation. This appears to be the most favorable system for the hydrogenation of arenes with organometallic catalysts described until now [181].

Silica-supported poly-γ-diphenylphosphinopropylsiloxane-Pt complex catalyzes the hydrogenation of aromatic hydrocarbons at 30°C and 1 bar. Hydrochloric acid promotes the reaction [182].

Metal carbonyls and related complexes were tested under various reaction conditions as catalysts for the hydrogenation of model-coal compounds [183]. Organometallic compounds of Ir, Rh and Mo showed good catalytic activity for the hydrogenation of a bituminous high-volatile coal at $\geq$ 380°C and 100 bar [184].

See also [127,136].

6. Hydrogenation of Carbonyl Compounds

Hindered aromatic ketones may be electrochemically reduced into α-glycols in an aprotic medium (DMF) on a Hg cathode in the presence of $MnCl_2$ [185].

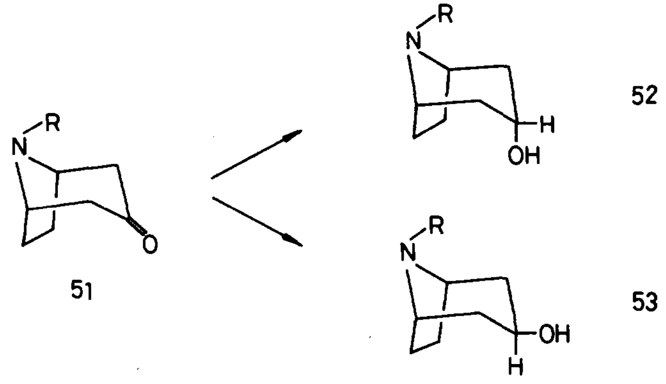
The hydrogenation of aldehydes and ketones with H_2 is catalyzed by $Fe(CO)_5$ as catalyst precursor if a tertiary amine is used as solvent. The actual catalyst system is probably $HFe(CO)_4^-$ and the protonated amine formed by the following equilibrium reaction [186]:

$$Fe(CO)_5 + H_2 + R_3N \rightleftharpoons HFe(CO)_4^- + HNR_3^+ + CO$$

Propionaldehyde was hydrogenated to propyl alcohol by use of Ru carboxylate complexes like $RuCl(OOCR)(PPh_3)_2$ (R = Me, Et, Ph or CH_2Cl). Electron-attracting substituents on the carboxylate group enhanced catalytic activity [187]. The reduction of benzaldehyde is catalyzed by $H_2Ru_4(CO)_{12}^{2-}$ at 125°C and 20 bar H_2 [88].

Hydrogenation of aldehydes to alcohols during hydroformylation of olefins with Co-based catalysts occurs above 160°C. The reaction is faster with linear than with branched aldehydes [188]. Carboxylic acids RCOOH are hydrogenated to the corresponding esters $RCOOCH_2R$ with H_2 + CO in the presence of $Co_2(CO)_8$ as catalyst precursor [68].

Rhodium complexes containing PPh_3 ligands and modified by Et_3N can be used as catalysts for the homogeneous hydrogenation of ketones. Kinetic experiments suggest, that the reaction between $HRh(PPh_3)_3$ and the ketone is the rate determining step of the catalytic cycle. The activity of the catalyst is not very sensitive to the structure of the substrate [189]. The hydrogenation of N-substituted nortropinones (51, R = alkyl, Ph, benzyl, Cy) with Rh-phosphine catalysts has been reported. Using PPh_3 as ligand the α-isomer alcohols (52, nortropines) were obtained with 85-98% selectivity. If the catalyst contained PBu_3 the β-isomer alcohols (53, norpseudotropines) were the main products in 88-100% yield [190].



In a related study, 4-t-butylcyclohexanone has been hydrogenated with various phosphinerhodium complexes formed <u>in situ</u> from $Rh_2(NBD)_2Cl_2$ and PR_3 as catalysts. Systems containing phosphines of high basicity form Rh(III) dihydrides and yield mainly the equatorial alcohol, systems obtained from less basic (aromatic) phosphines are only active in the presence of Et_3N under which conditions they form Rh(I) monohydrides and yield the thermodinamically less stable axial alcohol [191].

Pd complexes of silica-supported poly-γ-cyanopropylsiloxane and poly-γ-aminopropylsiloxane have been found to catalyze the hydrogenation of aldehydes and ketones under ambient conditions. The catalytic activities are greatly influenced by the N/Pd atomic ratio. The complexes are stable and can be reused [192].

See also [93,136,179].

7. Hydrogenation of Nitro Compounds

Reaction of $Co(dmg)_2.2H_2O$ with amines gives a catalyst for the hydrogenation of $PhNO_2$. Paramagnetic solutions of these catalysts were examined by ESR. Changes of the spectrum during the catalytic process indicate the formation of a bis(cobaloxime)-$PhNO_2$ intermediate complex during hydrogenation [193].

$Ru(PPh_3)_3Cl_2$ catalyzes the reduction of nitro compounds to amines with synthesis gas ($CO:H_2$ = 1:1) under phase transfer conditions at room temperature and atmospheric pressure. The reaction is less effective with CO alone (H coming in this case from the water solvent) while no reaction occurs using H_2 alone [194].

The hydrogenation of aromatic nitro compounds e.g. $PhNO_2$ and p-$ClC_6H_4NO_2$ with trans-$Pd(py)_2Cl_2$ in EtOH proceeds at room temperature and 1 bar to give amines in 60-94% yields [195]. Pd(II) chelates of alizarine salts form donor-acceptor complexes with nitroaromatic compounds. This result supports the peripheral mechanism of nitroaromatics hydrogenation catalyzed by chelates of group VIII metals with oxyquinones [196]. Pd complexes of silica-supported polyacrylonitrile and of silica-supported polyvinylpyrrolidone catalyze the hydrogenation of aromatic nitro compounds. The polyvinylpyrrolidone complex could be reused several times if small amounts of AcOH were added [197].

8. Miscellaneous Hydrogenations

The industrially important hydrodenitrogenation reaction performed with CoMo catalysts has been modelled under homogeneous conditions with $Rh_6(CO)_{16}$ as catalyst [198]. Acrylonitrile is hydrogenated to propionitrile at 90°C and 3 bar of H_2 with trans-$Rh(CO)(PPh_3)_2Cl$ as catalyst. In the presence of formaldehyde the reaction is faster and the deactivation of the catalyst is slower [199]. Hydrogenation of acrylonitrile is also catalyzed by $Ir(CO)(PPh_3)_2Cl$, in this case Cl^- inhibits the reaction. The dihydride $H_2Ir(CO)(PPh_3)_2Cl$ reacts stoichiometrically with acrylonitrile at 100°C to give propionitrile [200].

The selectivity of Pd(II)-phtalocyanine as hydrogenation catalyst depends on conditions and pretreatment. The catalyst is active for the hydrogenation of many types of double bonds under all conditions tested, but the hydrogenolytic activity (removal of halogens or benzyl groups) is influenced by the pH of the medium or the addition of $NaBH_4$ [201]. Benzyl derivatives $PhCH_2X$ (X = OH, OCH_2Ph, OMe, OAc) react with CO + H_2 at 220°C and 90-100 bar in the presence of $[Ru(CO)_3I_2]_2$ and aqueous HI to give toluene, HX and polymers of the type $H(C_7H_6)_nH$ (n = 2-6). Benzyl alcohol reacts by first forming dibenzyl ether which is then disproportionated to toluene and benzaldehyde and the latter is hydrogenated again to benzyl alcohol [202].

In the presence of the Mo(IV) dimer $[(\eta^5\text{-}CH_3C_5H_4)MoS]_2S_2CH_2$ carbon disulfide reacts with H_2 at 75°C and 2-3 bar to give H_2S and thioformaldehyde. The latter is stabilized by its interaction with the Mo complex forming $[(\eta^5\text{-}CH_3C_5H_4)Mo]_2(S_2CH_2)(S_3CH_2)$. This interaction is reversible: the latter complex dissociates in solution at 75°C into the original Mo dimer and trithiane. It also reacts with H_2 to yield a complex mixture of organic sulfur compounds [203].

See also [93, 136].

9. Coordination Chemistry Related to Hydrogenation

Dibenzo[a,e]cyclooctatetraene has been proposed as a selective poison suitable to distinguish homogeneous and heterogeneous hydrogenation catalysts. The distinction is made possible by the much larger sensitivity of the homogeneous catalysts as compared to that of the heterogeneous ones [204].

The mechanism of olefin insertion into the Rh-H bond has been studied by magnetization-transfer techniques on *trans*-$HRh(C_2H_4)(PPr^i_3)_2$ as model. The insertion reaction is preceeded by isomerization of the *trans* to the *cis* complex [205]:

$$\textit{trans}\text{-}HRh(C_2H_4)(PPr^i_3)_2 \rightleftharpoons \textit{cis}\text{-}HRh(C_2H_4)(PPr^i_3)_2 \rightleftharpoons EtRh(PPr^i_3)_2$$

The reactivity of 18 different alkyne- and vinylidene-substituted clusters towards H_2 has been studied under homogeneous conditions at 120°C. Alkynes, alkenes, alkanes and hydrogenolysis products and rearranged cluster frames were formed. The observations support hydrogenation processes occurring on clusters [206].

10. Dehydrogenation

The reduced clusters $[Mo_2Fe_6S_8(SPh)_9]^{4-,5-}$ and $[Fe_4S_4(SPh)_4]^{3-}$ evolve H_2 from PhSH in DMF solution at ambient temperature. The (5-) cluster also produces H_2 from Et_3NH^+ [207].

The most active catalyst hitherto known for the homogeneous dehydrogenation of iPrOH has been found to form from $Rh_2(OAc)_4$ by adding PPh_3 *in situ*. From the reaction solution a complex was isolated. Using this as a catalyst with PPh_3 and AcOH present no induction period was observed [208]. The dehydrogenation of racemic 1-phenylethanol by a Rh(I) - chiral phosphine catalyst was investigated at 170-195°C and the dependence of enantiomer differentiation on temperature determined [209].

Solutions of Rh(TPP)Cl in cyclohexanol or 2-propanol evolve H_2 when irradiated under Ar. The only products are the corresponding ketones and hydrogen formed stoichiometrically and therefore this is a clean photocatalytic dehydrogenation of secondary alcohols. Total turnover numbers of several thousand were obtained and the system is working with visible light which is important for the utilization of solar energy [210]. The complexes $HRh(PPr^i_3)_3$ or $HRh(CO)(PPr^i_3)_2$ catalyze the photochemical decomposition of primary alcohols RCH_2OH to H_2, CO and RH [211].

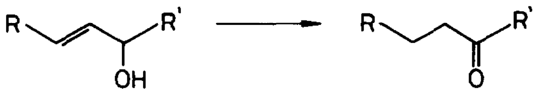
11. Hydrogen Transfer Reactions

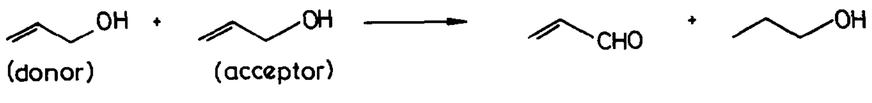
a) Alkanes as Hydrogen Donors

The rhenium hydrides $(Ar_3P)_2ReH_7$ (Ar = Ph, p-FC_6H_4, p-MeC_6H_4) catalyze the H-transfer from cycloalkanes to 3,3-dimethylbutene-1 as a H-acceptor at 30-80°C. The olefins are not formed by a radical process and once formed are not interconverted [212].

b) Hydrogenation of C=C Bonds

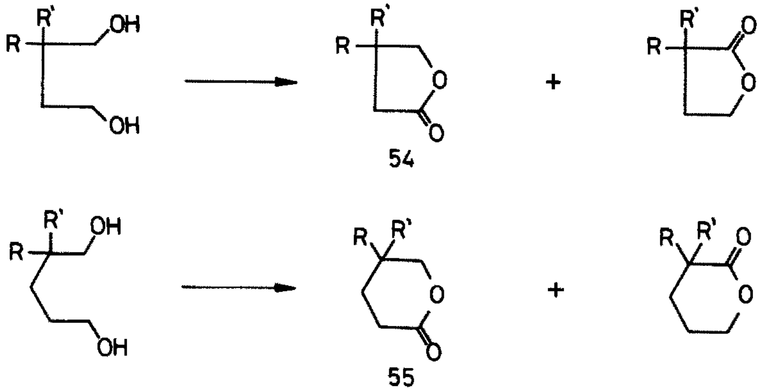
The dinitrogen complex trans-$Mo(N_2)_2(dppe)_2$ catalyzes the intra- and intermolecular hydrogen-transfer reactions of allylic alcohols:





In some cases, decarbonylation occurred giving cis-$Mo(CO)_2(dppe)_2$ and the hydrocarbon [213].

The dehydrogenation of unsymmetrically substituted 1,4- and 1,5-diols with Ru-phosphine complexes as catalysts and $PhCH{=}CHCOCH_3$ as H-acceptor proceeds regioselectively. Major products are β-substituted γ-lactones (54) and γ-substituted δ-lactones (55), respectively:



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The regioselectivities of the catalyst complexes were largely affected by their phosphine ligands: the complexes containing seven-membered chelating ligands like $Ru_2(dppb)_3Cl_4$ [dppb = $Ph_2P(CH_2)_4PPh_2$ showed higher regioselectivities than $Ru(PPh_3)_3Cl_2$ in each case [214].

$Co_2(CO)_8$ catalyzes the H-transfer from dihydroanthracene or 9-fluorenol to 1,1-diphenylethylene at 150°C under CO pressure. The reaction is probably radical in character and $HCo(CO)_4$ is the hydrogen-transferring species [215].

H-transfer from iPrOH to hexene-1 is catalyzed by $HRh(PPr^i_3)_3$ or $HRh(CO)(PPr^i_3)_2$ [211]. The transfer hydrogenation of different unsaturated ketones by several alcohols as H-donors has been investigated with $HRh(PPh_3)_4$ as catalyst. The mixing order of reactants influences catalyst activity. Highest rates can be achieved if the H-acceptor is added to the solution of the catalyst in the H-donor. Primary alcohols can also be used as apparently the catalyst is not poisoned by eventual decarbonylation of the aldehyde formed [216]. The catalyst hydrogenates the olefin also in a stoichiometric reaction. $Rh(PPh_3)_3$ is regarded as the principal active species in the system. Two parallel pathways were proposed which differ in the sense that either the donor or the acceptor reacts first with the Rh-phosphine complex [217,218].

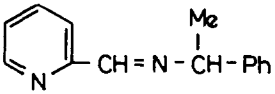
Polystyrene-anchored $IrCl(CO)(PPh_3)_2$ used as H-transfer catalyst for the reduction of olefinic double bonds by formic acid was investigated by mass spectrometry of the pyrolyzed beads. Evidence could be obtained for the formation of a π-olefin adduct [219].

c) Hydrogenation of C=O Bonds

In the homogeneous H transfer from α-phenylethanol to cyclohexanone catalyzed by $Ru(PPh_3)_3Cl_2$ in diphenyl ether as solvent the order of addition of donor, acceptor and catalyst have a pronounced effect on the rate of reaction. An induction period is observed [220,221]. The Rh(I) Schiff-base complexes $[Rh(TFB)(PyCH=NR)](ClO_4)$ [TFB = tetrafluorobenzobicyclo[2,2,2]octatriene, PyCH=NR = Schiff--base of pyridine-2-aldehyde, R = Bu, Cy, Ph and p-(Me,MeO,F or Br) phenyl] are catalysts for transfer of H from iPrOH to acetophenone in the presence of KOH. Activity increases with the basicity of the amine [222]. Complexes of the type $[Ir(L_2)(diene)]ClO_4$ and $Ir(L_2)(diene)X$ (L_2 = bpy, phen and substituted derivatives; X = Cl, Br, I) are active catalyst precursors in the presence of a base for the transfer hydrogenation of unhindered cyclohexanones by 2-propanol. In the case of 4-tBu-cyclohexanone the trans alcohol is the main product [223].

d) Asymmetric Hydrogen Transfer Reactions

The system formed in situ from $Rh_2(HD)_2Cl_2$ and the chiral Schiff-base (-)-(56) catalyzes the asymmetric transfer hydrogenation of ketones by isopropyl alcohol. Enantioselectivities up to 23% have been achieved [224].



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Asymmetric transfer hydrogenation of α,β-unsaturated carboxylic acids and esters with alcohols was carried out using $RuCl_2(PPh_3)_3$ or $Ru_2Cl_4L_3$ as catalyst (L = (+)- or (-)-DIOP) at 160-190°C. Optical purities of the products ranged between 1-26%. Chiral alcohols like α-D-glucofuranose derivatives usually enhanced asymmetric induction [225].

e) Hydrogen Transfer to N- or Halogen-containing Compounds

Complexes of the type $Ir(L_2)(ethylene)_2Cl$ and $[Ir(L_2)(HD)]ClO_4$ (where L_2 = bpy or phen) were used as catalyst precursors in the reduction of aromatic nitro compounds by H-transfer from iPrOH. Active catalysts were obtained in the presence of KOH. At a KOH/catalyst ratio of 1, amines were the main products whereas at high KOH/catalyst ratios hydrazo derivatives could be obtained with good selectivity [226]. Polystyrene-anchored $Rh(PPh_3)_3Cl$, $Ru(PPh_3)_3Cl_2$ and $Ir(CO)(PPh_3)_2Cl$ were shown to catalyze selective transfer hydrogenolysis of trichloromethyl compounds by iPrOH at 140-160°C. The chlorine content of the catalyst increases gradually during the process which leads to deactivation. The catalyst can be reactivated by treatment with air or O_2 [227].

f) Intramolecular Hydrogen Transfer

Benzaldehyde is transformed into benzyl benzoate under mild conditions using $HRh(PPh_3)_4$ as catalyst:

$$2\ PhCHO \longrightarrow PhCOOCH_2Ph$$

$HRh(PPh_3)_3$ is the catalytically active species and the rate determining step is the reaction of the second aldehyde molecule with the catalyst. Benzyl alcohol is formed as a byproduct in a stoichiometric hydrogenation reaction [228].

12. Reduction without Molecular Hydrogen

a) Transition Metal Hydrides

The Cu(I) complex $(triphos)Cu(BH_4)$ reduces CO_2, COS and CS_2 to give the formate, thioformate and dithioformate Cu(I) complexes (triphos)CuOCHO, (triphos)CuSCHO and (triphos)CuSCHS [229]. Polymer-supported $HFe(CO)_4^-$ can be prepared from $KHFe(CO)_4$ and an anion-exchange resin (Amberlyst A26) in its chloride form. It selectively reduces nitroarenes to amines with 75-92% yields [230]. The anionic cluster $HFe_3(CO)_{11}^-$ was supported on commercial poly(styrene-divinylbenzene) anion exchange resins reduces nitrobenzene to aniline in a stoichiometric reaction. The proton source are unknown support impurities. Infrared spectra suggest that the complex $HFe_3(CO)_9NPh^-$ is an intermediate of the reduction [231].

b) Low Valent Transition Metal Complexes

Reduction of (57) with aqueous $TiCl_3$ and acetone gave (58) in 93% yield. The observed regioselectivity of the reduction is ascribed to an ortho effect [232].

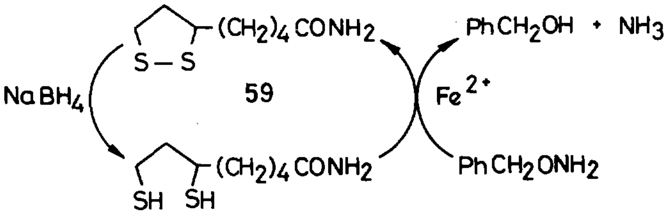
57 58

The tetrachloroalkanes $RCHClCH_2CCl_3$ (R = Bu, pentyl) are reduced to trichloroalkanes $RCHClCH_2CHCl_2$ by $Fe(CO)_5$ + $(Me_2N)_3PO$ at 140°C [233].

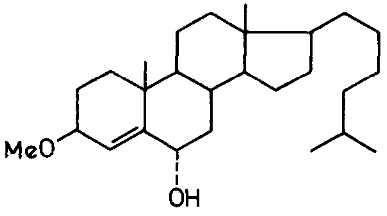
c) Inorganic Reductants in the Presence of Transition Metal Complexes

Several aromatic and aliphatic nitro compounds were reduced to the corresponding amines in excellent yields by the Ti(II) species generated by the reduction of $TiCl_4$ with amalgamated Mg. Chloro, cyano, and allyl carboxylate groups were not affected [234]. Molybdenum(IV) complexes of the sequential polypeptides $(Gly_2Cys)_n$ and $(Gly_3Cys)_n$ catalyze the reduction of acetylene by $NaBH_4$. Ethylene, ethane and butadiene are formed [235].

Lipoamide (59) and Fe(II) catalyze the reduction of O-benzylhydroxylamine with $NaBH_4$ in a carbonate buffer (pH 9.8) and EtOH (1:1) at 30°C. The following catalytic cycle has been proposed for this reaction [236]:



Diphenylacetylene is reduced to cis- and trans-stilbene by $NaBH_4$ in the presence of $Co(PPh_3)_3Cl$ in THF solution. The same system catalyzes the isomerization of cis-stilbene to the trans isomer [237]. The olefinic double bonds in (60) and (61) were reduced using cob(I)alamin as catalyst, aqueous AcOH as solvent and metallic Zn as electron source [238]:



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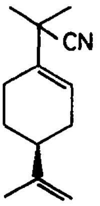

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The $NaBH_4$ + $PdCl_2$ + polyethylene glycol + CH_2Cl_2 system has been found to be effective for the hydrogenation of acetylenic triple bonds to the corresponding alkenes at 10°C. This is the first example of the hydrogenation of acetylenes using $NaBH_4$ [239]. Allylic acetates like (62) can be reductively cleaved by polymethylhydrosiloxane (PMHS) in the presence of Pd(0) complexes as catalysts to yield olefins. The reduction is highly chemoselective, for example α, β-unsaturated carbonyl compounds do not interfere [240].

62

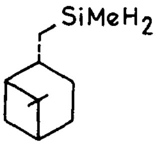
The reduction of alkyl iodides to alkanes is catalyzed by Pt^{2+} in aqueous solutions containing NaI and $HClO_4$. An RPt(IV) complex has been proposed as an intermediate [241-243]. The platinum cluster carbonyl anion $[Pt_{12}(CO)_{24}]^{2-}$ catalyzes the reaction between water and p-benzoquinone:

If O_2 is purged from the system more than 20 moles of hydroquinone may be obtained per mole of cluster despite the fact that the reaction is endothermic (+27.1 kcal mol^{-1}) [244].

See also [249].

d) Reduction of Carbonyl Compounds via Hydrosilylation

Hydrosilylation of prochiral ketones with (62a) and $Rh(PPh_3)_3Cl$ as catalyst followed by hydrolysis gave optically active alcohols with 9-26% optical yield [245]. Hydrosilylation of acetophenone with H_2SiPh_2 in the presence of a catalyst obtained in situ from $Rh_2(COD)_2Cl_2$ and the chiral thiazolidine (63) followed by hydrolysis yields (R)-α-phenylethanol with 72-87% o.y. The ligand (63) can be obtained from L-cysteine methyl ester and 2-pyridine carbaldehyde as a mixture of diastereomers and may be used as such [246].



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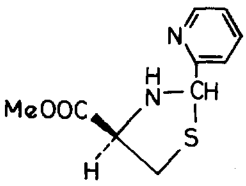

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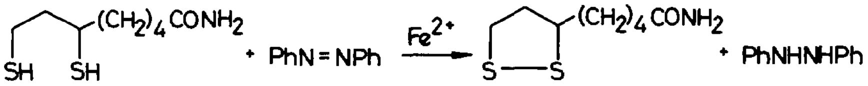
e) Organic Reductants in the Presence of Transition Metal Complexes

Phenyldiazonium chloride was reduced to benzene in MeOH in the presence of $(dppe)_2Mo(N_2)(L)$ (L = N_2,CO) or $(dppe)_2W(CO)_2$ as catalyst. The H atom came from the Me group of MeOH [247].

Dihydrolipoamide (64) in the presence of Fe^{2+} ions was found to be an effective reagent for the reduction of azobenzene to hydrazobenzene and of nitrobenzene, nitrosobenzene or phenylhydroxylamine to aniline in good yields under mild conditions [248].



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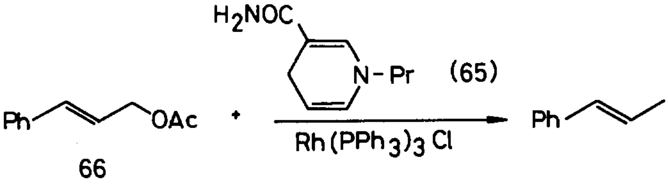
Complexes of Co(dmg)$_2$ with thiourea, selenourea or PPh$_3$ added to the reductants (rongalite C or NaHSO$_3$) used for the fixation of vat dyes accelerate the process [249]. The rate of reduction of indigo carmine by rongalite in the presence of Co glyoxime complexes is proportional to catalyst concentration. The efficiency of the catalyst depends mainly an the axial ligands [250].

The NAD(P)H model compound N-propyl-1,4-dihydronicotinamide (65) reduces cinnamyl acetate (66) to trans - β -methylstyrene in 97% yield in the presence of Rh(PPh$_3$)$_3$Cl at 70°C:



No reduction takes place in the absence of the transition metal complex and aliphatic allyl acetates are inert even in the presence of the Rh complex [251].

The reduction of 1-heptene to heptane by formic acid is catalyzed by tpm complexes of Rh, Pt and Pd at 80-100°C. The activity of the catalysts increases in the order Pd < Pt < Rh [252].

f) Photochemically Assisted Reduction

Photoreduction of methylviologen (MV^{2+}) by several Ru(II)L$_3$ complexes (L = bpy, bipyrazine and similar ligands) was studied in the presence of triethanolamine in aqueous solution. Quantum yield of MV$^+$ formation was 0.98 when L = 2,2'-bipyrazine [253].

g) Electroreduction

Imines were reduced to amines by the clusters Fe$_4$S$_4$(SR)$_4^{3-}$ (R = Ph, p-ClC$_6$H$_4$, CH$_2$Ph) in MeCN/MeOH solution. The clusters were generated from Fe$_4$S$_4$(SR)$_4^{2-}$ electrolytically [254].

IV. Oxidation

1. Catalytic Oxidation of Hydrocarbons or Hydrocarbon Groups with O_2

a) General

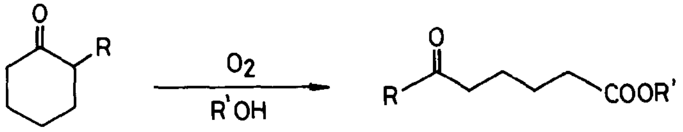
The catalytic activity of metal ions for the autoxidation of hydrocarbons was found to be related to their activity in catalyzing the decomposition of tBuOOH [255].

b) Oxidation of Alkanes

The ratio of monohydroperoxides to bifunctional hydroperoxides formed during the oxidation of decane with O_2 using different transition metal stearates as catalysts has been determined [256].

Addition of $Mn(OAc)_2$ in the liquid-phase oxidation of n-butane at 165°C and about 50 bar decreased butane conversion and increased the yield of carboxylic acids and esters [257]. Partial substitution of Mn by Ce in a K-Mn catalyst for the liquid-phase oxidation of pentadecane increased the rate without decreasing the selectivity [258]. The oxidation of n-pentane in the liquid phase was investigated without a catalyst and in the presence of Fe, Ni, Co, Cr, and Mn ions. Mn ions exerted the largest effect increasing the selectivity for HCOOH and the rate of molecular decomposition of hydroperoxide intermediates [259].

Saturated hydrocarbons can be oxidized by a system containing iron powder and a carboxylic acid in aqueous pyridine under O_2. Oxidation takes place preferentially at methylene groups giving secondary alcohols and ketones. This is to be expected from reactions involving insertion of a coordinatively unsaturated transition metal complex into the C-H bond of an alkane. An iron complex could be isolated from the reaction mixture [260]. In a similar system, adamantane could be oxidized to adamantanols and adamantanone by O_2 at room temperature using a catalyst composed of iron powder, $Na_2S.9H_2O$, AcOH and H_2O [261]. Ferric salts like $FeCl_3$ catalyze the regiospecific oxygenation of cycloalkanones (66a) by O_2 to give oxo esters (66b) in the presence of aliphatic alcohols at 60°C. The catalyst probably activates both the substrate and O_2 simultaneously. Starting from 2-methyl- or 2-ethylcyclohexanone yields up to 93% could be achieved [262].



66a 66b

The complex $Fe_3O(OAc)_6py_{3.5}$ catalyzes the oxidation of saturated hydrocarbons by O_2 in the presence of Zn and AcOH in pyridine as solvent at 30-40°C. The ratio of tertiary H to secondary H substitution in adamantane is not in accord with either an oxenoid or a free radical mechanism [263].

The influence of O_2 pressure and catalyst concentration on the rate and selectivity of octane oxidation in the presence of a Co salt as catalyst has been investigated [264].

The oxidation of methane by oxygen to MeOH an MeCl is catalyzed by Pt(II) and Pt(IV) salts and $Na_8HPMo_6V_6O_{40}$. Methanol undergoes further oxidation under the reaction conditions [265].

It was shown, than in the liquid-phase oxidation of methyl isobutyrate $Cu(OAc)_2$ affects only the initiation step and does not participate in propagation and termination [266].

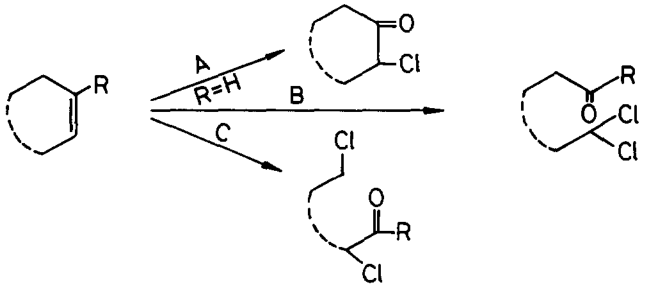
See also [290].

c) Oxidation of Olefins

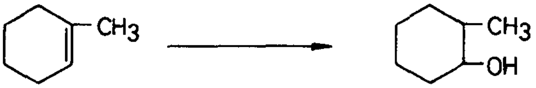
Olefins were oxidized by O_2 in the presence of Mn TPP Cl and $NaBH_4$. Alcohols and ketones were formed [267].

Photooxidation of cyclic olefins in pyridine in the presence of $FeCl_3$ produces either α-chloro ketones (route A), gem-dichloro ketones (route B) or α,ω-dichloro ketones (route C) depending upon the substitution pattern of the substrate olefin (see next page). The synthetic utility of route B was demonstrated by the synthesis of some natural products [268].

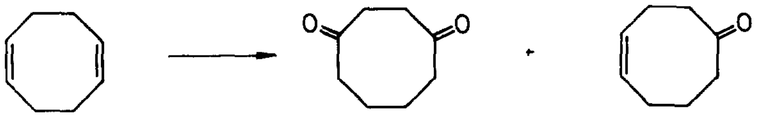
The equimolar mixture of aqueous OsO_4 and a solution of bovine serum albumin (BSA) react with emulsified α-methylstyrene to form a complex of 2-phenylpropane-1,2-diolatodioxo-osmium(VI) with BSA. This complex catalyzes the enantioselective oxidation of α-methylstyrene to (S)-2-phenylpropane-1,2-diol (o.y. 68%) [269].



The liquid-phase oxidation of cyclohexene is catalyzed simultaneously by Co complexes and $MoO_2(acac)_2$. A mechanism has been proposed [270]. The oxygenation of olefins with O_2 and $NaBH_4$ using octaethylporphirinatorhodium(III) as catalyst provides a new route to anti-Markownikoff alcohols. Thus 1-methylcyclohexene gives 2-methylcyclohexanol as the highly regioselective product:



Catalyst turnover number is about 200 [271]. Rh(I) complexes like $Rh(PPh_3)_3Cl$ catalyze the oxygenation of olefins to give carbonyl compounds by C=C bond cleavage. For example, 2,3-dimethyl-2-butene is transformed into acetone [272]. The Rh complexes $[Rh(PSR)_2](BF_4)$ ($PSR = Ph_2PCH_2CH_2SR$; R = Ph, Me, Et) react with O_2 to give the corresponding 1/1 adducts $[Rh(PSR)_2O_2](BF_4)$. These oxygen complexes react with 1-alkenes and methyl ketones are formed. In the presence of added acid oxygen transfer becomes catalytic [273]. The oxidation of 1-hexene to 2-hexanone by O_2 is catalyzed by the $[Rh(CO)_2(solvent)](BF)_4$ + Cu(II) system. Chloride considerably increases catalyst stability. The results indicate that a Rh(III) chloride complex is the catalyst or the immediate precursor [274]. Cyclo-octane-1,4--dione (67) is formed from COD and O_2 in benzene solutions containing PPh_3 and catalytic amounts of $Rh(PPh_3)_3Cl$ or $Rh(PPh_3)_3(O_2)Cl$:



67 major 67a minor

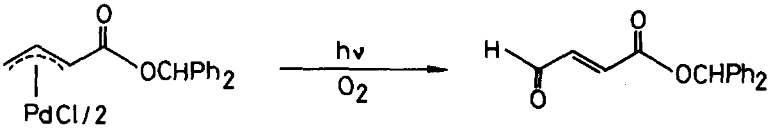
This is the first example of a homo-co-oxygenation at two olefinic centers in one molecule. As minor byproducts the monoketone (67a) and $OPPh_3$ are formed in a hetero-co-oxigenation reaction [275].

Dimethylacetamide solutions of $[HIr(COD)Cl_2]_2$ catalyze the simultaneous oxidation of cyclooctene to cyclooctanone and H_2 to water:

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

The overall reaction shows similarities to catalytic oxydation reactions performed by a class of P450 enzymes. Oxygen is transferred to the olefin probably via a hydroperoxy (IrOOH) intermediate, the resulting hydroxo species is thought to be transformed back into the hydride by H_2. Turnover for cyclooctanone per Ir is about 2/day [276].

Irradiation of oxygenated solutions of η^3-allylpalladium complexes, (e.g. 68) formed from alkenes substituted in α- or β-position by an electron-withdrawing group, leads to a regioselective oxidation of the allyl group [277].



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Terminal olefins can be converted into ketones by O_2 at 80°C and atmospheric pressure in a benzene/water two-phase reaction mixture using a $PdCl_2$ + $CuCl_2$ catalyst and a phase transfer catalyst like cetyltrimethylammonium bromide. With quaternary ammonium salts containing alkyl groups of shorter chain length than 12 C atoms, little or no oxidation occurs [278]. Instead of Pd, complexes of Ru and Rh may be used as catalysts too and in this case short-chain quaternary ammonium salts are equally effective [279]. The oxidation of n-butenes to ethyl methyl ketone by O_2 and $PdCl_2$ as catalyst in aqueous solution is second order in Pd suggesting a binuclear complex as intermediate [280]. The oxidation of styrene to acetophenone is catalyzed by $Pd(tmp)_2Cl_2.3H_2O$ in aqueous solution in the presence of $CuCl_2$ [281].

Octene-1 reacts with O_2 in the presence of the $Pt(PPh_3)_2O_2+CO_2$ adduct to produce autoxidation products and 2-octanone. Labelling the adduct with ^{18}O shows that reaction with peroxy oxygen is not directly involved [282].

The oxidation of propylene to propylene glycol acetates is catalyzed by $CuCl_2$ and I_2 in AcOH solution. The results indicate that $CuCl_2.I_2.C_3H_6$ and $CuCl.CuCl_2.I_2.C_3H_6$ are formed as intermediates [283, 284].

See also [285, 286, 288, 289, 329, 332].

d) Epoxidation of Olefins

In the cooxidation of olefins with Mo complexes like $(PhEt)Mo(Et_2C_6H_4)$ or Cp_2MoCl_2 the complexes are oxidized to $MoO_{3.8}.CH_2$ which catalyzes the oxidation of olefins to hydroperoxides. The latter react with the olefins to form epoxides [285]. The influence of $MoO_2(acac)_2$, MoO_3 and $Co(acac)_3$ on the liquid phase oxidation of cis- and trans-4-octene with O_2 at 110°C was studied. The yield of epoxides was increased in the presence of Mo complexes, but the Co complex only increased the rate of autoxidation [286]. The novel oxoperoxomolybdenum(VI) complexes $MoO(O_2)L_2Cl_2$ (L = DMF, HMPA) stoichiometrically oxidize olefins to epoxides and consecutively to cleavage products. Since these complexes are prepared from the corresponding cis-dioxomolybdenum(VI) complexes $MoO_2L_2Cl_2$ and Ph_3COOH, and the dioxo complexes catalyze the epoxidation of olefins by Ph_3COOH, it is very probable that similar peroxo complexes are involved as reactive intermediates in the catalytic system [287].

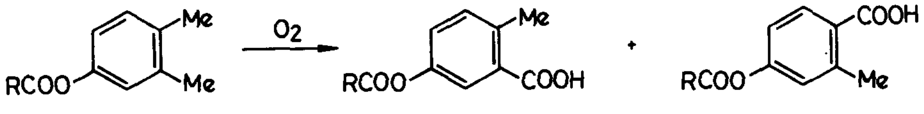
The liquid-phase oxidation of cyclohexene is catalyzed by layered compounds of graphite with $CuCl_2$, $CoCl_2$, $MnCl_2$, $FeCl_3$, $FeCl_2$, $NiCl_2$ or $MoCl_5$. The $MoCl_5$ containing catalyst yields significant amounts of cyclohexene oxide [288]. The activity of a $MoCl_5$-laminated graphite catalyst was higher than that of $MoCl_5$ alone. Both catalysts operate by a radical chain mechanism as judged by the products formed (epoxide, cyclohexanol and cyclohexene hydroperoxide) [289].

A biphasic H_2O - C_6H_6 system containing (TTP)MnCl and a phase transfer agent as catalysts and ascorbate as a reducing agent, activates O_2 leading to selective epoxidation of olefins and oxidation of alkanes to ketones and aldehydes at room temperature. The selectivity of epoxidation crucially depends on the presence of ascorbate and the phase transfer agent which efficiently inhibit autoxidation leading to enols and enones [290].

e) Oxidation of Aromatics

The oxidation of fluorene, anthracene and phenanthrene with a Co^{2+} + $Mn^{2+}.Br^-$ catalyst was investigated. A mechanism has been proposed according which the catalyst first reacts with O_2 to form a complex and then this complex reacts with the substrate [291]. Activation energies were determined for the oxidation of phenanthrene anthracene and fluorene with the same (Co:Mn:Br = 9.5.5:10) catalyst. The selectivity for acid products was highest for fluorene and lowest for anthracene [292].

Kinetic data were obtained for the oxidation of xylenes in the presence of Co^{2+}, Mn^{2+} and Cu^{2+} complexes with dicarboxylic cation exchange resins. At 80-120°C the main products were monofunctional alcohols, aldehydes and carboxylic acids [293]. The liquid-phase oxidation of 4-stearoyl-o-xylene (69) (R = $nC_{17}H_{35}$) with a Co-Mn catalyst produced the monocarboxylic acids (70) and (71) at temperatures $\leq$ 80°C. The dicarboxylic acid could not be prepared because at higher temperatures the stearoyl group was split off [294].

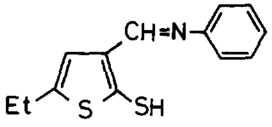


69 70 71

The catalytic activity of Ru(III), Mn(III) and Co(II)-carboxylates in the liquid-phase oxidation of p-xylene increased in the order stated. The low activity of Ru(III) resulted from the blocking of the coordination sites by the reaction products [295]. Different metal phthalocyanines were tested as catalysts in the oxidation of methylbenzenes by O_2. Activity order was found to be $Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+}$ [296].

Mixed Cu-Fe polyphtalocyanines have been used as catalysts of cumene oxidation. Their Mössbauer spectra show, that the presence of Cu ions influences the distribution of Fe species and their ability to undergo oxidative destruction to Fe oxides [297].

Zirconyl chloride accelerates the $CoBr_2$-catalyzed oxidation of toluene [298]. The Co complex of the thiophene derivative (72) exhibited both catalytic and inhibiting activity in cumene oxidation. The Ni complex of the benzothiophene derivative (73) showed this dual activity in decane oxidation [299].



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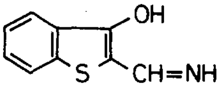

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Oxidation of benzene with air in aqueous sulphuric acid in the presence of cuprous salts produces phenol. Under optimum conditions the yield of phenol was 8.3% based on the cuprous salt (CuCl) added. Addition of H_2O_2 increased the phenol yield [300]. Liquid-phase oxidation of anthracene to anthraquinone by O_2 in the presence of copper salts was investigated. The 1:1 $Cu(OAc)_2$ + KBr catalyst system was found to be the most active [301]. Benzene can be oxidized to phenol and hydroquinone with O_2 in the presence of Cu^+-ions. The oxidation can be performed in a continuous manner if the Cu^+-ions are regenerated electrochemically [302].

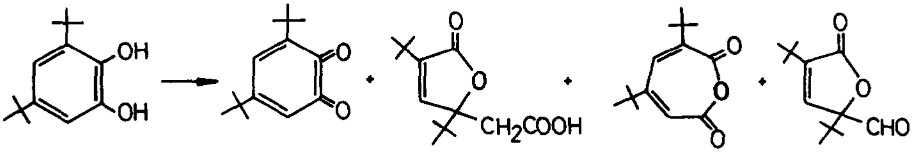
2. Catalytic Oxidation of O-containing Functional Groups with O_2

a) Oxidation of Alcohols

The kinetics of the liquid-phase oxidation of benzyl alcohol catalyzed by cobalt acetate and NaBr was investigated. The reaction is zero order in alcohol and 1.5 order in catalyst [303]. Mixtures of $CpCo(S_2CNMe_2)NO_2$ or $CpCo(S_2CNMe_2)NO_3$ and $BF_3.Et_2O$ oxidize benzyl alcohol to benzaldehyde in a stoichiometric reaction. In the presence of O_2 the oxidation becomes catalytic in the case of the nitrate species. A mechanism in which NO_2^- reacts with BF_3 to give the actual oxidant has been proposed [304].

b) Oxidation of Phenols

Phenol and anisole are hydroxylated by air with an Fe^{2+}/EDTA catalyst combined with electrochemical reduction. At low conversion monohydroxylation is the principal reaction, at higher conversions polyhydroxylated aromatics are the main products [305]. The oxygenation of 3,5-di tert-butyl catechol (74) is catalyzed by the Fe(III) complex formed in situ from $FeCl_3$, bpy and py. A wide range of products is formed (75-82). The quinone (75) is not oxygenated by the iron complex [306].



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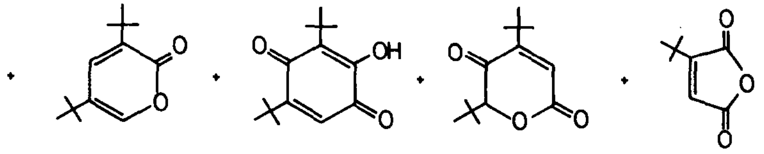
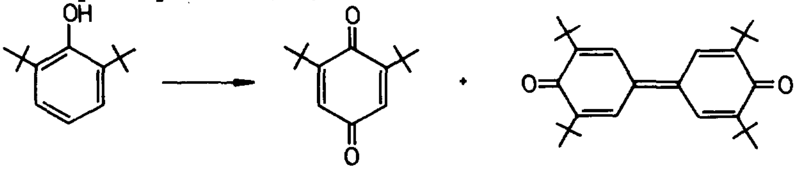


79 80 81 82

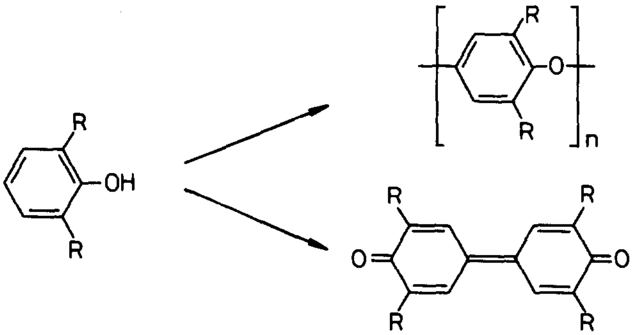
Cobaloxime derivatives of the type $Co(Hdmg)_2L_n$ (L = PPh_3, py, Et_3N; n = 1,2) are active catalysts of dehydrogenation and O insertion reactions of phenols, amines, phosphines, isonitriles and nitroso compounds at room temperature and 1 bar O_2 pressure. H_2O_2 is not an intermediate in these reactions and spectroscopic data suggest successive O-atom transfer from superoxocobaloxime(III) and μ-peroxodicobaloxime(III) to the substrates [307]. The peroxo complex $Co(bpy)_2(\mu\text{-}O_2)(\mu\text{-}OH)Co(bpy)_2^{3+}$ catalyzes the oxidation of 2,6-di tert-butyl phenol (83) by O_2. The corresponding benzoquinone (84) and diphenoquinone (85) are formed:



83 84 85

The reaction is first order in the complex and first order in phenol. A mechanism has been proposed [308].

The oxidation of 3,5-di(tert-butyl)catechol (74) by O_2 to quinone is catalyzed by Cu(II) complexes of β, δ-triketones like 2,4,6-heptatrienone and β-ketophenols like o-acetoacetylphenol Binuclear complexes are more active than mononuclear ones [309]. Autoxidation of tert-butylphenols is catalyzed by N-substituted ethylenediamine complexes of Cu(II). Catalytic activity increases with sterical crowding around the nitrogen atoms. Oxidation products are mostly substituted biphenyls [310]. The species $Cu_4py_4Cl_4O_2$ which is an active initiator for phenolic oxidative coupling is transformed by pyridine into $Cu_2py_2Cl_2$ and $[py_mCuO]_n$. The tetrameric complex is regarded as the catalyst for the oxidative dimerization of phenols into diphenoquinones (87) whereas the $[py_mCuO]_n$ polymers initiate the formation of polymeric products (86). This explains the influence of pyridine on product distribution [311].



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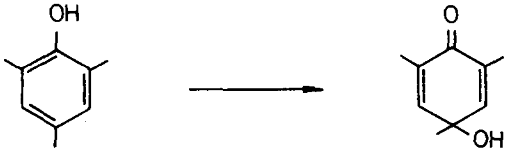
87

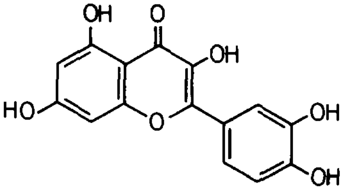
The crystal structure of the catalytic precursor in the oxidation of phenols with O_2, $Cu_2Cl_2py_2(OMe)_2$, has been determined [312]. Oxidation of phenols by O_2 in the presence of $Cu_4Cl_4O_2(MeCN)_4$ gives selectively oxidative coupling products, if the Cu/phenol ratio is low or para-hydroxylation products, if this ratio is high. In the latter case phenols unsubstituted in the para position (88) yield p-quinones (89) whereas p-substituted phenols (90) are transformed into p-quinols (91) [313].

88 → 89



90 → 91

Complexation constants of quercetin (92) with Co(II), Ni(II), Cu(II) and Zn(II) ions in ethanol-water mixtures were determined. The structures of these complexes and possible mechanisms were discussed for oxidation of (92) with O_2 catalyzed by metal ions [314].



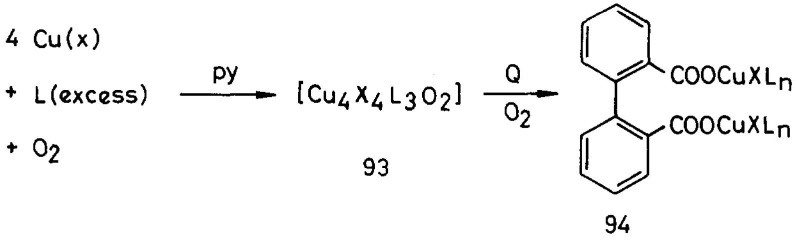
92

See also [323].

c) Oxidation of Aldehydes, Ketones and Quinones

The kinetics of acetaldehyde oxidation by O_2 in the presence of Co acetate was studied. Under conditions of kinetic control the rate was 0.5 order in Co^{3+} and 1.4 order in acetaldehyde. Theoretical analysis and the results suggest that $CH_3CO_3^{\bullet}$ is the main free radical in the liquid phase [315]. Optimal conditions were determined for the liquid-phase oxidation of butyraldehyde to butyric acid and its anhydride in a continuous flow reactor under O_2 pressure in the presence of a Cu and Co acetate catalyst [316]. The kinetics of the liquid-phase oxidation of p-carbomethoxybenzaldehyde with O_2 in the presence of Co dicaprylate as catalyst was determined [317].

The autoxidation of benzaldehyde catalyzed by $Co(OAc)_2.H_2O$ and NaBr is an oscillating reaction. The periodical changes of the redox potential (and the color) of the solution can be followed for several hours [318]. A mechanism was suggested to account for this oscillation. It is proposed that in one stage of the reaction benzoyl radical reacts primarily with O_2, while in the second, benzoyl is oxidized by Co^{3+}. An essential feature of the oscillations is the periodic depletion of dissolved oxygen [319]. The oxygenolysis of 9,10-phenanthrenequinone(Q) by CuXL complexes (X = Cl,Br; L = py,phen,bpy) to the diphenato-complexes (94) has been reported. Copper-dioxygen complexes of the type (93) are the intermediates of this reaction [320].



d) Miscellaneous Oxidations

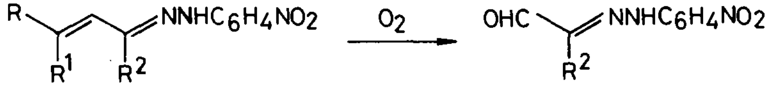
The oxidation of cyclic acetals by O_2 was investigated in the presence of Co^{2+}, Cr^{3+} and Fe^{3+} salts. The activities of these catalysts decreased in the stated order while the activities of the substrates increased in the order 1,3-dioxane < 1,3-dioxepanes < 1,3-dioxolanes [321]. The stereoselective oxidation of L-ascorbate is catalyzed by Fe(III) complexes of poly(Na D- or L-glutamate). The H^+ concentration is a critical parameter of the reaction [322]. Three $Ru(NH_3)_5^{3+}$ groups can be attached to sperm whale myoglobin which drastically changes the oxidation-reduction properties of the protein. This modified heme protein ("Ru_3Mb") effectively catalyzes the oxidation of ascorbate and hydroquinone by O_2 [323]. Azole-metal complexes were investigated as catalysts for the oxidation of ascorbate. In DMF as solvent, the activity decreased with the nature of the metal in the order $Ni^{2+} > Cu^{2+} > Co^{2+}$. The rate of oxidation varied with the solvent, DMF was found to be the best and DMSO, EtOH and H_2O resulted in lower rates [324].

High temperature wet oxidation of woods with O_2 leads to the production of a mixture of organic acids. Ferric sulfate increases the yield of formic acid but decreases the yield of acetic acid and methanol [325].

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

If the oxidation of N,N-dimethylaniline with H_2O_2 and Fe(II) as catalyst is carried out under oxygen, O_2 is consumed. N-Dealkylation and nuclear hydroxylation are observed [326]. Tertiary amines are catalytically oxidized to amine oxides by O_2 with $RuCl_3.xH_2O$ in aqueous acetone. Yields never exceed 50%, the other 50% of the amine is oxidized to carboxylic acids and secondary amines [327].

Co complexes of mesoporphirin IX and tetrakis(p-sulfophenyl) porphine catalyze the oxidation of adrenaline (151) by O_2 [328]. Oxygenation of 4-nitrophenylhydrazones of α, β-enones (95) with Co(salpr) (96) as catalyst results in the oxidative cleavage of the double bond [329].



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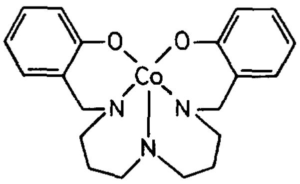

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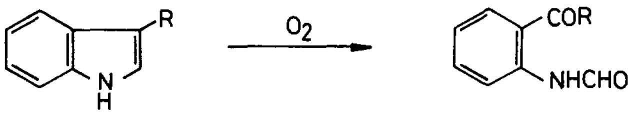
In the Co(II)(salen)-catalyzed oxygenolysis of 3-substituted indoles (97) the actual catalytic species has been found to be the Co(III)(salen) complex (98) of an anion of the product. The rate determining step is the H^+ transfer from the substrate to the product anion which takes place in the coordination sphere of the catalyst. Accordingly, catalysis involves activation of the substrate but not that of O_2 [330].



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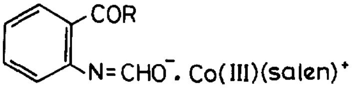

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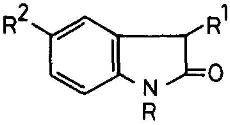
Oxidation of 2-indolinones (99) with O_2 in the presence of Co-Schiff base complexes gave 4 different products (100-103). R, R^1 and R^2 may be H, Me or Ph [331].



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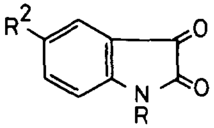

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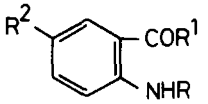

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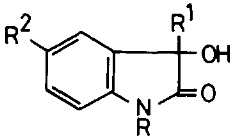

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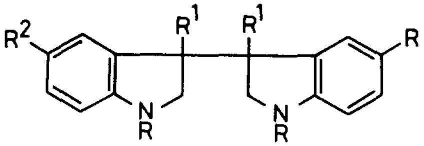


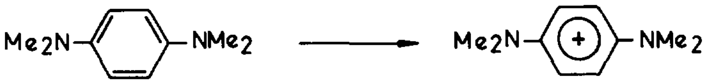
103

Oxidation of amino alkenes with O_2 catalyzed by $PdCl_2$ + $CuCl_2$ in aqueous solution ("Wacker process conditions") yields several products depending on the structure of the amine. Thus primary amines are cyclized to pyrrolines (104) while tertiary amines give amino ketones (105) [332].

104

105

The oxidation of tetramethyl-p-phenylenediamine (106) by O_2 is catalyzed by binuclear Cu(II) complexes. The activity of the catalysts is high if the ligands have a flexible bridge and flexible chelating groups like in [107]. Such a structure enables the catalyst to assume a conformation which is favorable for the formation of an intermediate complex with O_2 and (106) [333].



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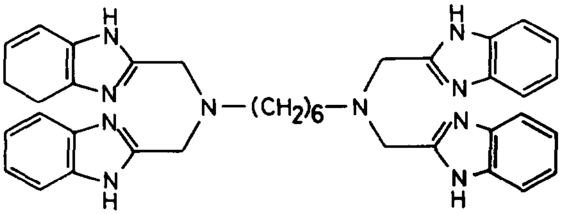


107

Triarylketenimines $Ph_2C{=}C{=}NC_6H_4R$-p (R = OMe, Me, H, Cl) undergo oxygenolysis in the presence of $CuCl_2$ to yield benzophenone, isocyanates and isonitriles. The ratio of products varies with the substituents, the rates follow the order OMe > Me > H > Cl [334].

See also [307].

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

Fe(III) complexes of the type FeX_3 and $Fe(OPPh_3)_2X_3$ (X = Cl, Br, NCS) catalyze the oxidation of PPh_3 to $OPPh_3$ by O_2 [335].The simultaneous oxidation of CO and PPh_3 by O_2 is catalyzed by $Rh_6(CO)_{16}$. During catalysis dinuclear and tetranuclear Rh-PPh_3-CO complexes are formed. As confirmation of this declusterification, $Rh_4(CO)_{12}$ also catalyzes the reaction and the same intermediates are formed [336]. Some polyhedral closoborate salts of Pd(II)-PPh_3 complexes are active catalysts for the oxidation of PPh_3 by O_2,but are inactive for both hydrogenation or oxidation of acetaldehyde [337].

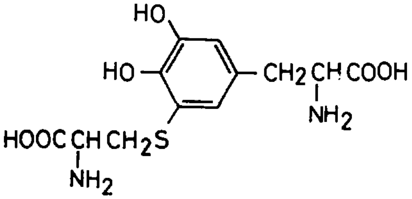
The kinetics of the Fe^{2+}-catalyzed oxidation of cysteine in aqueous solution in the presence of NaOH has been determined. A mechanism based on a 2-electron transfer from cysteine to oxygen has been proposed [338]. The kinetics of oxidation of cysteine by O_2 catalyzed by the iron containing ion exchange resin KB-4 was studied in aqueous solution at 20-50°C [339]. The oxidation of glutathione (GSH) by O_2 in the presence of iron salts has been studied. An intermediate red complex has been observed which is proposed to be $(Fe^{3+}\text{-}SG)_2O_2^{2-}$. A scheme for the catalytic cycle has been presented [340].

Brominated amino, hydroxy, nitro or sulfo derivatives of Co phthalocyanine are more effective catalysts for the oxidation of thiols with O_2 than their nonbrominated analogs [341]. The oxidation of Et_2NCS_2Na to $(Et_2NCS)_2S$ is catalyzed by substituted derivatives of Co octahydrooxyanthraquinonecyanine. Rate constants and activation energies were determined [342].

Isothiocyanates can be oxidized by $PdCl_2$ and O_2 to isocyanates:

$$R\text{-}NCS + PdCl_2 + O_2 \longrightarrow R\text{-}NCO + Pd + SOCl_2$$

If $CuCl_2$ is added to the reaction mixture the oxidation becomes catalytic in palladium [343]. The Cu^{2+}-catalyzed autoxidation of cysteinyldopa (108) has been studied [344].



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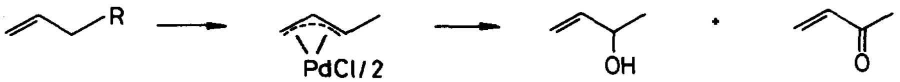
The oxidation of o-chlorotoluene in AcOH catalyzed by Co acetate and NaBr is accompanied by the formation of organic Br-containing compounds [345].

See also [275, 307].

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

a) Oxidation of Hydrocarbons or Hydrocarbon Groups

Acetylacetonates, sterates and caproates of V, Cr, Mn, Fe, Co and Cu and carbonyls of Cr, Mn and Rh catalyze the oxidation of nonane, cyclohexane and Ph_2CH_2 by tBuOOH to give ketones [346]. Cyclohexane was oxidized by ozone in the presence of Mn, Co and Cr compounds as catalysts. The activity of these increased in the order $Co(st)_2 < Mn(acac)_3 < Cr(OAc)_3 < Cr(st)_3 < Co(acac)_3$ $Cr(CO)_6$ [347]. π-allyl-Pd complexes (110) which can be easily prepared from olefins (109) are regioselectively hydroxylated by tBuOOH and $Mo(acac)_2O_2$ as catalyst to allyl alcohols (111). As byproducts enones (112) are formed in minor amounts [348].



109 110 111 112

The kinetics of the Mn(II)-catalyzed oxidation of α, β-unsaturated carboxylic acids by bromate has been determined in aqueous AcOH and H_2SO_4. The initial process is composed of two reactions: the first is a comparatively slow one and the second is a fast reaction which is mainly oxidation by Br_2. Latter can be prevented by the addition of $Hg(OAc)_2$ [349]. The hydroxylation of unactivated alkanes has been observed in a catalytic system containing iodosylbenzene and various iron porphyrins. Highest alcohol yields were usually obtained using tetra-o-porphyrin as ligand. The mechanism proposed involves initial oxidation of the iron porphyrin, H abstraction from the alkane and rapid collapse of this radical to give the product alcohol and regenerate the iron(III) catalyst [350]. Mono- and disubstituted alkenes are converted to trans-vicinal diacetates by heating an acetic acid solution of ammonium persulfate and a $FeSO_4.7H_2O$ catalyst. Yields range between 12-95%. Co(II), Ag(I), Cu(II) and Mn(II) salts are less effective [351]. The hydroxylation of benzene with H_2O_2 in the presence of Fe^{3+} produces phenol in only very low yields. It has now been found that using quinones as cocatalysts the yield of phenol is increased up to 41% [352].

The use of Ru(III) as a homogeneous catalyst changes the kinetics of trans-stilbene oxidation by $Tl(OAc)_3$ in aqueous AcOH [353]. Aromatic and heteroaromatic acetates (113) have been oxidized to dicarboxylic acids (114) by aqueous $NaIO_4$ in the presence of catalytic quantities of RuO_4. The method can be used to establish the absolute configurations of the starting alcohols [354].

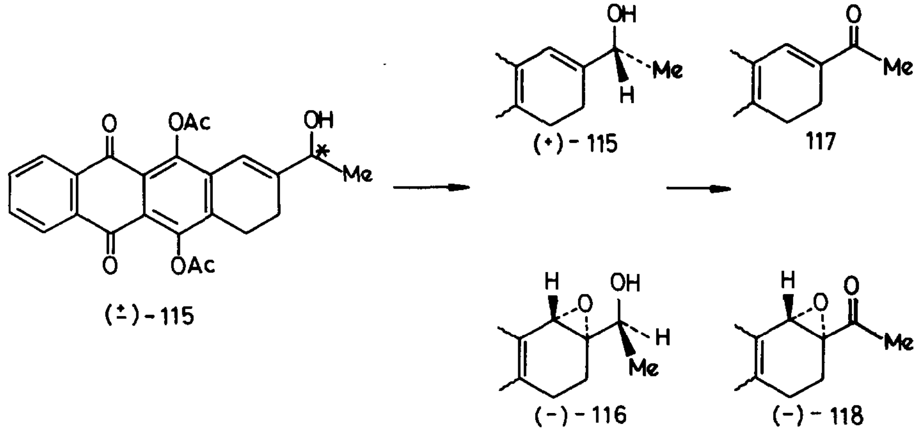
113 114

The hydroxylation of α, β-unsaturated esters bearing a γ-OH function by N-methylmorpholine oxide and catalyzed by OsO_4 leads to 3,4-dihydroxy-γ-lactones with remarkable stereoselectivity [355].

The oxidation of 2-substituted anthracenes to anthraquinones with tBuOOH is catalyzed by $Rh(PPh_3)_3Cl$ with 50-90% yields. This catalyst is more efficient than $VO(acac)_2$ and lower yields result also if the oxidation is carried out stoichiometrically with CrO_3 [356]. The oxidation of ethylene with nitric acid in acetic acid solutions to ethylene glycol monoacetate was studied in the presence of Pd(II) compounds as catalysts. An intermediate containing nitrite ion and ethylene coordinated to Pd was suggested [357]. The oxidation of propylene by benzoyl peroxide to allyl acetate is catalyzed by $Pd_4(phen)(OAc)_2$ in AcOH at 60°C [358].

b) Epoxidation of Olefins

Sharpless epoxidation of (±)-(113) with tBuOOH in the presence of $Ti(OPr^i)_4$ afforded a kinetically resolved mixture of (±)-(115) and (-)-(116). The above mixture was oxidized with chromic acid in a two-phase system to give (117) and (-)-(118) [359]:



(±)-115 (+)-115 117 (−)-116 (−)-118

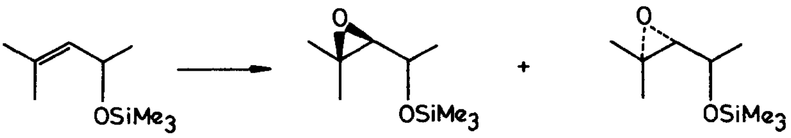
The Z,Z-diene (119) was epoxidized enantioselectively by tBuOOH in the presence of $Ti(OPr^i)_4$ and (+)-dimethyl tartrate to give the epoxide (120) which was then oxidized into the aldehyde (121) by CrO_3 in py and dichloromethane (Collins oxidation) [360]:

119

R = CH_2OH , 120

R = CHO , 121

A kinetic study of the epoxidation of cyclohexene by ethylbenzene hydroperoxide in the presence of V(III) and V(IV) acetylacetonates suggests the formation of two different catalyst-hydroperoxide complexes [361]. Trimethylsilyl ethers of allyl or homoallyl alcohols [e.g.(122)] are epoxidized with $tBuOOSiMe_3$ and a catalyst system consisting of vanadyl acetoacetate and tris(trimethylsilyl) phosphate. The stereoselectivities fall roughly between those obtained with tBuOOH/V-catalyst and m-chloroperbenzoic acid oxidation [362].



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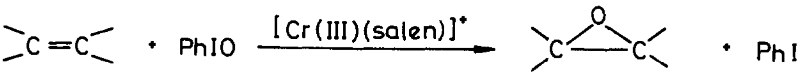
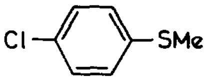
The reaction of E-geraniol (123) with tBuOOH in the presence of polymer-anchored V^{5+} or Mo^{6+} complexes gave 2,3-epoxygeraniol (124) in up to 98% yield. The catalysts were prepared from $NaVO_3$ or K_2MoO_4 solutions and styrene-divinylbenzene resins modified by bis(phosphonomethyl)amino or bis(2-hydroxyethyl)amino groups [363].


123 124

The oxochromium(V) complex $O{=}Cr(salen)^{+}PF_6^{-}$ has been prepared by treating the corresponding Cr(III) complex with iodosylbenzene. The oxo complex transfers its oxygen atom to alkenes or phosphines, yielding epoxides or phosphineoxides, respectively. Since the oxochromium(V) species can be easily regenerated this allows the following catalytic reaction [364]:



The epoxidation of olefins with H_2O_2 and a $MoO_2(acac)_2$ + $(Bu_3Sn)_2O$ catalyst was studied in iPrOH. The active species is $MoO_2(OSnBu_3)_2$ [365]. The rates of oxidation of two sulfides (125) and (126), and epoxidation rates of two olefins (127) and (128 = geraniol) by tBuOOH and H_2O_2 in the presence of V^{5+} and Mo^{4+} catalysts have been measured. Based on the kinetic data and the Arrhenius parameters the role of the OH group in these oxidations has been discussed [366]. The epoxidation of (127) and (128) was



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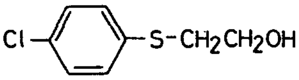

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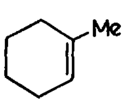

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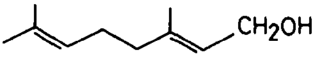

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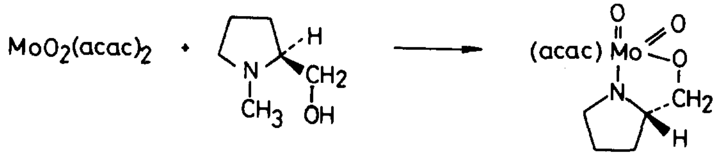
also studied in different solvents (EtOH and dichloromethane) and in the presence of HMPA. The results confirm the electrophilic character of the oxygen transfer process [367]. Molybdenum-containing cation exchange resins based on Amberlite IRC-84 were used as catalysts for the epoxidation of propylene with tBuOOH [368]. The epoxidation of cyclohexene by ROOH is catalyzed by Mo, V, W and Ti cyclohexanediolates. The activity of the catalysts decreases in the order stated and the activity of the oxidant decreases with R according $PhCHMe > PhCMe_2 > Me_3 > Me_2CEt$ [369]. In the epoxidation of olefins by PhCH(OOH)Me the Mo naphtenate catalyst is deactivated mainly by peroxy radicals formed in the decomposition of the hydroperoxyde. This effect is especially important if the selectivity of epoxidation is low and thus parallel to epoxidation the radical decomposition of hydroperoxyde is significant [370].

The yield of propylene oxide in the epoxidation of propylene with isopropylbenzene hydroperoxide and a Mo propylene glycolate catalyst is increased if 2,2',6,6'-tetramethylpyridine-1-oxyl is added which inhibits the thermocatalytic decomposition of the hydroperoxide [371]. The effect of various additives was investigated on the selectivity of propylene oxide formation from propylene by epoxidation with ethylbenzene hydroperoxide in the presence of Mo complexes as catalysts. The kinetics of propylene oxide ring cleavage by α -phenyl ethanol was determined [372]. The catalytic activity in the epoxidation of 1-hexene by isopropylbenzene hydroperoxide decreases in the following order:

$Na_3PMo_{12}O_{40} \sim AlPMo_{12}O_{40} > Na_4PMo_{11}VO_{40} > Na_4SiMo_{12}O_{43} \gg Na_3PW_{12}O_{40}$.
The selectivity for 1-hexene oxide is nearly 100% [373].

Epoxidation of 1-nonene with ethylbenzene hydroperoxide and a catalyst containing Mo and Li stearates was achieved with 80% selectivity at 83% conversion [374]. The complexes $(dppeH_2)(MoOCl_5)$, $MoOCl_3(dppe)$ and $Mo_2O_{2.5}Cl_5(dppe)_2$ were used to catalyze the epoxidation of cyclohexene by cumene hydroperoxide. All complexes are transformed under the reaction conditions into $MoO_2L_2(dppeO_2)$ (L = 1,2-cyclohexanediol) which was found to be the active catalyst [375]. Epoxidation of 3-methyl-2-buten-1-ol with cumene hydroperoxide catalyzed by $MoO_2(acac)_2$ in the presence of L-N-methylprolinol (129) yields epoxy alcohol of 50% optical purity at low conversions. The enantioselectivity of the reaction decreases with increase in conversion. This is due to the destruction of the chirality of the catalyst (130) formed from $MoO_2(acac)_2$ and (129), either via oxidation of the chiral ligand or its replacement by product alcohols [376].



129 130

The epoxidation of styrene by aralkyl hydroperoxides in the presence of Mo naphtenate was described by a mathematical model [377].

The epoxidation of olefins by H_2O_2 is efficiently catalyzed by the two-component system consisting of WO_4^{2-} and PO_4^{3-} (or AsO_4^{3-}) ions. The reaction is run in a two-phase system (water/dichloroethane) and in the presence of a phase transfer catalyst. 80-90% yields are achieved [378].

Di- and trisubstituted olefins are epoxidized with good yields (40-85%) with NaOCl in the presence of Mn(TTP)OAc. The selectivity of the reaction is modified by pyridine. Without pyridine *cis*-stilbene gives a mixture of *cis* and *trans* epoxides with the *trans* as the predominant species, the addition of pyridine reverses this ratio and up to 94% *cis* isomer may be obtained [379]. The epoxidation of norbornene (131) with the NaOCl/Mn(TPP)OAc system gives the *exo*-product (132). The *syn*-addition of the O atom is also confirmed in the case of carene (133) yielding the α-epoxide (134). In both cases the epoxidation occurs therefore with the same stereochemistry as that observed with peracids suggesting that chlorohydrins are not intermediates in this catalytic epoxidation [380]:

131 132

133 134

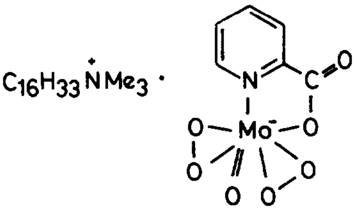
Tetra-*para*-substituted Mn(TPP)OAc was anchored onto a helical polymer of L-tyrosine isocyanide and used as catalyst for the epoxidation of cyclohexene with NaOCl in a two-liquid-phase system. Pyridine and substituted pyridines considerably enhanced the activity of the catalyst. The anchored catalyst was about three times as active as the non-anchored one [381].

The epoxidation of olefins by iodosylbenzene is catalyzed by synthetic iron porphyrins. For example, with Fe(TPP)Cl cyclohexadiene oxide was produced in 93% yield. *Cis* olefins were found to be more reactive than *trans* olefins. The results suggest an approach of the double bond from the side of the iron-bound oxygen and parallel to the porphyrin plane [382]. If the porphyrins are modified to include optically active functionalities at the meso positions, asymmetric epoxidation can be achieved. Thus, using the Fe(III) complex of $5\alpha,10\beta,15\alpha,20\beta$-tetrakis (o-(R)-hydratropamidophenyl) porphyrin, styrene was oxidized by iodosylbenzene into (R)-(+)-styrene-oxide in 31% o.y. [383]. The $Fe(ClO_4)_3 + H_2O_2$ + MeCN system was used for the oxidation of cholesteryl acetate, *cis* and *trans* stilbene and adamantane. Epoxidations and radical oxidation processes were observed [384].

See also [399].

c) Oxidation of O-containing Functional Groups

The anionic picolinato Mo(VI) peroxo complex with cetyltrimethylammonium cation as counter-ion (135) has been found to oxidize secondary alcohols in water solution and to act as a catalyst of the oxidation of the same substrates at 50-70°C by H_2O_2. Ketones are formed in good yields. Organic sulfides are smoothly and quantitatively oxidized to sulfoxides [385].



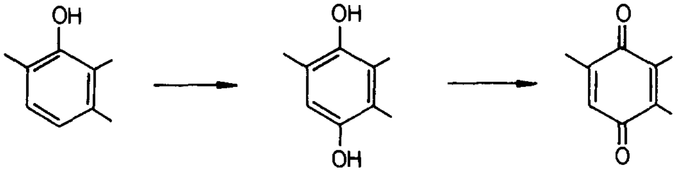
135

Oxidation of malic acid by $KBrO_3$ in the presence or absence of Mn(II) ions was studied in $HOAc-H_2O$ containing $Hg(OAc)_2$ and H_2SO_4

or $HClO_4$. Based on kinetic experiments a free radical mechanism has been proposed for the catalyzed reaction [386].

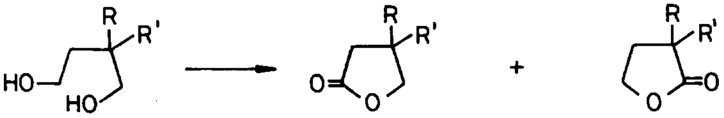
The Fe^{2+}-catalyzed oxidations of iPrOH to acetone by peroxyacetic acid or by H_2O_2 were compared. The peracid reaction is considerably faster than the H_2O_2 oxidation under similar conditions and does not yield detactable amounts of 2,5-hexanediol as byproduct [387]. Ascorbic acid is oxidized by H_2O_2 in the presence of $Fe_3O(AcO)_6(H_2O)_3^+$. A mechanism has been proposed according to which the anion of ascorbic acid is complexed by the catalyst and the oxidation proceeds by a chain mechanism. The oxidized and reduced forms of the catalyst are chain carriers, substrate radicals are not involved [388]. Fe(tetrapyridyl)$(OH)_2^+$ ions anchored to poly-L-glutamate catalyze the oxidation of L-ascorbate anion, L-DOPA and L-adrenaline by H_2O_2 at pH 7. These complexes serve as models for metalloenzymes, e.g. peroxidases and catalase [389].

The kinetics of MeOH and EtOH oxidation by alkaline $Fe(CN)_6^{3-}$ with Ru(VI) as catalyst was found to be zero order in oxidant and first order in alcohol and Ru [390]. A Ru(VI) hydride species was suggested as intermediate [391]. Oxidation of alcohols to carbonyl compounds by $Me_3SiOOSiMe_3$ is catalyzed by pyridinium dichromate or $Ru(PPh_3)_3Cl_2$. The Cr-containing system is equally effective for primary and secondary alcohols whereas the Ru-containing system selectively oxidizes primary alcohols in the presence of secondary alcohols [392]. The oxidation of phenols (136) to the corresponding p-quinones (138) by H_2O_2 is efficiently catalyzed by $RuCl_3$. The reaction proceeds over hydroquinones (137) as intermediates [393]:



136 137 138

Benzyl ethers are oxidized to benzoates by $NaIO_4$ in the presence of $RuO_2.xH_2O$ in high yield. This ruthenium tetraoxide oxidation procedure can be used for the preparative removal of the benzyl group [394]. The kinetics of oxidation of iPrOH by IO_4^- in the presence of Os(VIII), Ru(III) and their mixtures was studied. The catalytic effect was in the order Os < Ru < Os-Ru mixtures [395]. Oxidation of 2-substituted 1,4-butanediols (139) to the corresponding γ-butyrolacetones by the combination of Br_2 and Ni(II) alkanoates occurs with a high degree of selectivity at the 4-position (140≫141). The selectivity increases with increasing steric bulk of the alkanoates [396].

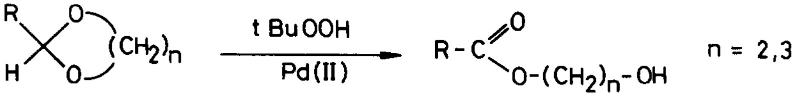


139 140 141

Saturated and unsaturated alcohols are oxidized to the corresponding ketones in good yields by using an aryl halide (PhBr or mesityl bromide) as an oxidant and $Pd(PPh_3)_4$ or $Pd(OAc)_2$ as a catalyst in the presence of a base (NaH or K_2CO_3):

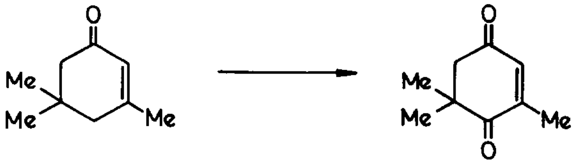
$$R_2CHOM + ArBr \xrightarrow{Pd} R_2CO + ArH + MBr \qquad (M = Na,K)$$

Oxidation of primary alcohols provides the corresponding aldehydes and/or esters [397]. The reaction of five- or six-membered cyclic acetals (142) with tBuOOH in the presence of a Pd(II) catalyst gives monoesters of diols (143) in good yield. $Pd(OOCCF_3)(OOBu^t)$ was found to be the most effective in promoting the reaction [398].



142 143

Oxidation of α-isophorone (144) with tBuOOH in the presence of Pd(II) or Cu(I) catalysts gives ketoisophorone (145) selectively. Similarly, the silyl enol ether (146) derived from (144) affords 6-hydroxylisophorone (147) [399].



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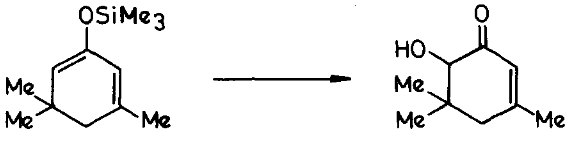
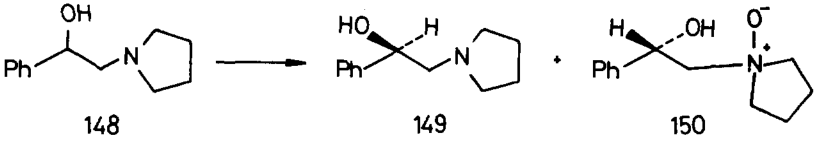


146 147

The kinetics and mechanism of the Cu(II)-catalyzed oxidation of lactic acid with N-chloro-p-toluenesulfonamide (chloramine T) has been investigated in alkaline solutions [400].

d) Oxidation of N-containing Compounds

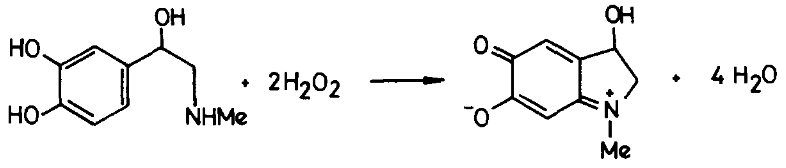
The enantioselective olefin-epoxidation catalyst composed of $Ti(OPr^i)_4$, tBuOOH, and diisopropyltartarate has been successfully used for the asymmetric oxidation of β-hydroxy amines (148) to N-oxides (150). The system works by the principle of kinetic resolution and if the natural tartrate ester is employed, the slow reacting enantiomer is always that related to (149) [401].



148 149 150

The phen and bpy complexes of Mn(II) catalyze the oxidation of p-toluidine by periodate. In weakly acidic solutions it is Mn(III) which reacts with p-toluidine [402].

The oxidation of L-phenylalanine by H_2O_2 in the presence of ferrous sulfate as catalyst was studied. Based on kinetic data two reaction schemes involving the HO$^•$ radical were proposed [403]. Oxidation of indole-3-acetic acid with H_2O_2 and Fe^{2+} ions was investigated [404]. The oxidation of adrenaline (151) to adrenochrome (152) by H_2O_2 is catalyzed by $FeL(OH)_2^+$ (L = 2,2':6',2":6",2'''-quaterpyridyl) anchored to polyglutamate. The kinetics of the reaction has been studied. Stereoselectivity is chiefly controlled by kinetic parameters [405].



151 152

Oxidation of phenylhydrazine to 4-hydroxyazobenzene by Ni(IV) was investigated in the presence of catalytic amounts of Cu(II). Kinetic results indicate the breakdown of Cu(II)-phenylhydrazine complexes to be rate determining [406]. $RCH_2CH_2NH_2$ (R = Pr, Bu, hexyl) are oxidized by $Na_2S_2O_8$ + $CuCl_2$ to form RCH_2CN as the main product and $RCCl_2CHO$, RCH_2COOH, and RCH_2CH_2Cl as minor products. Aldimines are intermediates [407].

See also [326, 389].

e) Oxidation of P- or S-containing Compounds

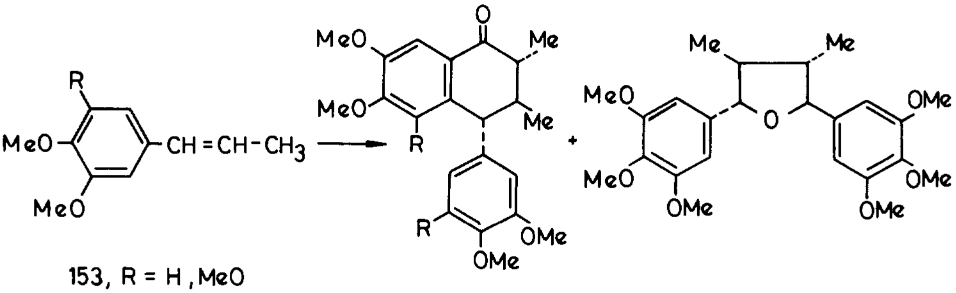
$MoO_2(S_2CNEt_2)_2$ was anchored on functionalized polystyrene and used to catalyze the oxidation of Me_2SO to Me_2SO_2 and cyclohexene to cyclohexene oxide with tBuOOH. The polymer-supported system gave better yields of the epoxide than the homogeneous counterpart [408]. Arylmethyl sulfides are oxidized to sulfoxides and cyclohexene to the corresponding epoxide by H_2O_2 in ethanol solution in the presence of $WO_5.HMPA.H_2O$ as catalyst. The reaction is first order in the substrate and in the catalyst and zero order in hydrogen peroxide [409]. Sulfides are oxidized to sulfoxides in high yields at room temperature by $(NBu_4)(IO_4)$ in the presence of Fe(TPP)Cl as catalyst. The analogous Mn-porphyrin complex was much less effective [410].

See also [364, 366, 385].

6. Stoichiometric Oxidation with High Valent Transition Metal Complexes

a) Oxidation of Hydrocarbons or Hydrocarbon Groups

Different 11- and 15-oxygenated steroids were obtained by oxidizing 3β -acetoxy-5 α-cholesta-8,14-diene with various amounts of chromic acid in aqueous sulfuric acid (Jones reagent) or performing the reaction under different temperatures [411]. Oxidation of substituted propenylbenzenes (153) by the new reagent systems CrO_3 + HBF_4 (or $HClO_4$) + MeCN gave the aryltetralones (154) and the tetrahydrofuran (155). If sulphuric acid was used, only the corresponding aldehydes were formed [412].



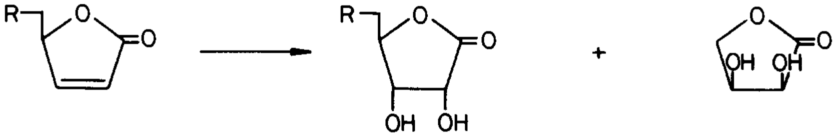
153, R = H,MeO

154

155

The oxidation of ^{14}C-3-propionic acid by Cr(VI) in H_2SO_4 or 85% H_3PO_4 furnishes mainly AcOH and CO_2 but one part of the propionic acid is directly oxidized to CO_2 [413].

The kinetics of the oxidation of malonic acid by Mn(III) in H_2SO_4 has been studied [414]. Alkanes and cycloalkanes were oxidized by acidic $KMnO_4$ solutions. Although $HMnO_4$ was about 1000 times more active than MnO_4^- the substrate selectivities and H/D isotope effects were similar [415]. Poly(ethylene glycol) ethers were found to be efficient and recoverable phase transfer agents in oxidations with $KMnO_4$. In a benzene-water two-phase system octene-1 was oxidized to heptanoic acid in 59% yield [416]. Oxidation of γ-butenolides (156) with $KMnO_4$ in CH_2Cl_2 in the presence of crown ether affords the corresponding 2,3-cis-dihydroxy-γ-butyrolactones (157,158) in high yields (27-88%). High stereoselectivity in favor of the lactones (157) was observed if bulky substituents R were introduced at the γ-position of the butenolides [417]:



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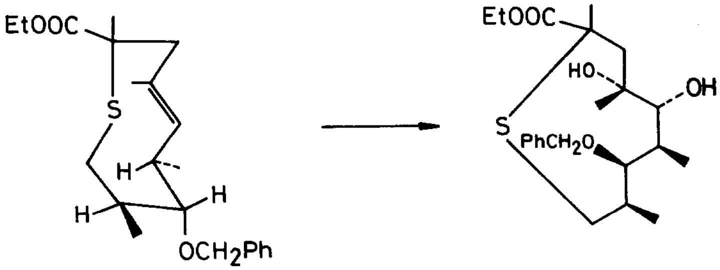
158

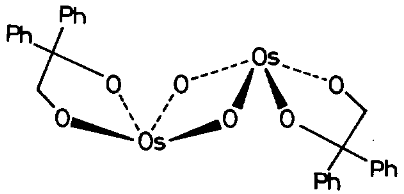
R = e.g. nBu, PhCOO, Ph_3CO

Oxidation of the alkene (159) with OsO_4 in py ("osmylation") at room temperature affords the diol (160) in 75% yield [418]:



159 160

Osmylation of di- or trisubstituted cyclic C_{10-15} (Z)-alkenes having an α-alkyl substituent and that of α-branched E trisubstituted cyclic alkenes occurs with high stereoselectivity. The structure of the dihydroxylated products is in agreement with least hindered attack by OsO_4 on a conformer of the olefin which has the allylic substituent in pseudoequatorial position [419]. Intermediates of the oxidation of 1,1-diphenylethylene with OsO_4 were identified as dimeric Os(VI) esters like (161) with dioxametallacyclopentane rings [420].



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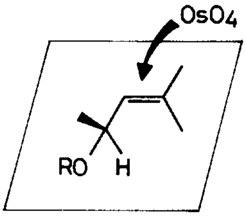
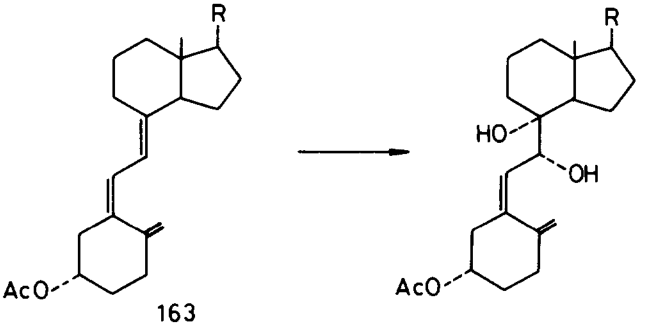
An empirical formulation has been proposed to predict the major hydroxylated products obtained in the OsO_4 oxidation (stoichiometric or catalytic) of allylic alcohol systems. Accordingly, the stereochemistry of the major product is formulated as arising from the preferential approach of OsO_4 to the face of the olefinic bond opposite to that of the preexisting hydroxyl or alkoxyl group (162) [421]. Several examples compiled from the literature demonstrate the consistency of this formulation [422].



162

Highly regioselective cis-hydroxylations of 25-hydroxycholecalciferol (163) and its 3,5-cyclo derivative (164) by OsO_4 have been described [423].



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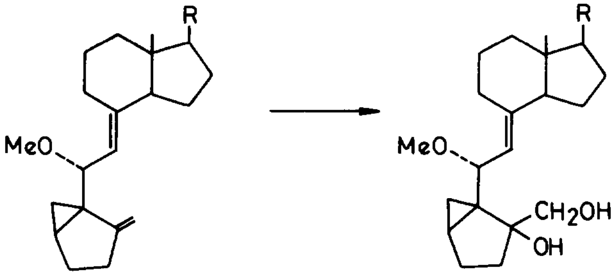
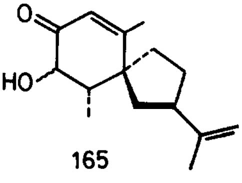


164

A kinetic study of the oxidation of p-methoxytoluene to the α-acetoxy derivative by Co(III)$W_{12}O_{40}^{5-}$ in acetic acid/water has been performed. A relatively strong isotope effect k_H/k_D = 5-7 has been observed. The rate data are best represented by a mechanism involving a reversible electron-transfer step, followed by the rate-determining proton abstraction from the radical cation [424].

The oxygen adducts $Rh(PPh_3)_2(O_2)X$ (X = Cl, NCO, NCS) decompose in benzene solution in the presence of 1-octene to yield hexyl-methyl ketone and Ph_3PO. This stoichiometric reaction models the initial phase of the Rh-catalyzed hetero co-oxygenation of terminal alkenes [425]. The Rh-nitro complexes $[(bpy)(MeCN)_2Rh(NO_2)](PF)_6$ and $[(MeCN)_4Rh(NO_2)](PF)_6$ oxidize ethylene or terminal olefins to acetaldehyde or alkanones, respectively. The corresponding nitrosyl complexes are formed but these can not be reoxidized under the conditions required for olefin oxidation to the nitro complexes and accordingly the oxidation can not be made catalytic. Thy bpy-containing complex also requires the presence of $(PhCN)_2PdCl_2$, an olefin activator [426].

The kinetics of the oxidative dehydrogenation of saturated hydrocarbons by Pd(II) in sulfuric acid has been studied. The cleavage of C-H bonds is regarded as the rate-determining step [427]. The oxidation of ethylene by $Na[Pd(NO_2)(NH_2)Cl_2]$ in MeCN and dioxane has been studied. The reaction is accelerated by dry HCl. In dioxane, two ethylene-Pd complexes with different configurations are formed [428]. The reaction of $Na_2[Pd(NO_2)Cl_3]$ with ethylene in absolute ethanol produces labile Pd-nitrosyl complexes and the ethylene is oxidized to acetaldehyde [429]. The oxidation of toluene by Pd(I) complexes in $PdSO_4$-H_2SO_4 solutions has been studied. Addition of benzene inhibits the reactions. Two routes involving Pd(I) and Pd(II) were distinguished [430]. Alkenes are oxidized to glycol derivatives in AcOH with $Pd(OAc)_2$ and $LiXO_3$ (X = Cl,Br,I). In case of ethylene and $LiBrO_3$ the following products were identified: $BrCH_2CH_2OAc$, $HOCH_2CH_2OAc$, $AcOCH_2CH_2OAc$, $HOCH_2CH_2OH$, CH_2=CHOAc and CH_3CHO. The selectivity for glycol derivatives was 82% [431]. Oxidation of the epimeric 3-hydroxysolavetivones (165) with $Cu(OAc)_2$ in refluxing methanol gave (166) in essentially quantitative yield. Performing the same oxidation with basic ferric chloride resulted in a mixture of (166) and (167)[432].



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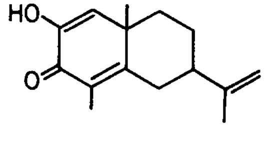

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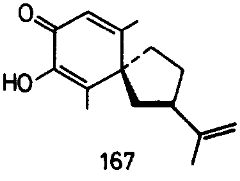


167

See also [356, 433, 446, 472]

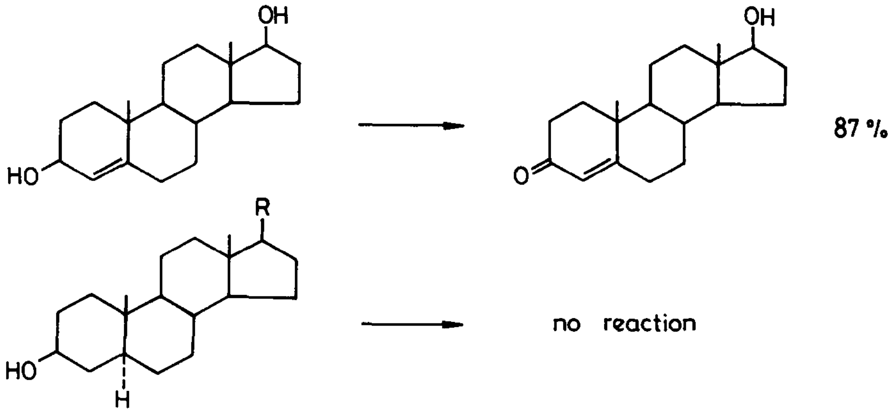
b) Epoxidation of Olefins

Vanadium(V) oxo peroxo complexes of the type $VO(O_2)(Pic)LL'$ ($L,L' = H_2O$, MeOH, monodentate or bidentate basic ligands; Pic = = pyridine-2-carboxylate) or $VO(O_2)(Pic)_2^-A^+L$ ($L = H_2O$, HMPA; $A^+ = H^+, PPh_4^+$) are effective oxidants in nonprotic solvents under mild conditions. They transform olefins into epoxides (and cleavage products), aromatic hydrocarbons to phenols and alkanes to alcohols and ketones. Alkanes are much less readily hydroxylated than aromatics and the reaction occures with a significant amount of epimerization at the hydroxylated carbon atom [433]. Chromyl nitrate converts olefins stereospecifically and with high selectivities into epoxides in aprotic media under mild conditions. The presence of cosolvents like DMF, acetone or py is necessary since these effect the reduction of the reagent to an oxochromium(V) species which itself is the active epoxidizing agent. In acetate, the epoxide is transformed into the corresponding alkene ketal [434]. The reaction of Cp_2MoX_2 (X = Cl,Br) with tBuOOH gives $(Cp_2MoX_2)^+(OOBu^t)^-$ which reacts with cyclohexene to give cyclohexene oxide [435].

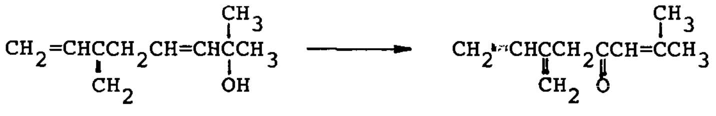
c) Oxidation of O-containing Functional Groups

Oxidation of 2,6-xylenol by acidic solutions of V^{5+} was studied in the presence of both added MeCN and AcOH. The reaction is much faster in AcOH. The reactions are second order in V^{5+} and the main products are monomeric and dimeric quinones [436]. The kinetics of the oxidation of tetramethylolmethane and 2,2-diethyl-1,3-propanediol with vanadium(V) was studied in H_2SO_4 and $HClO_4$ solutions [437].

Pyridinium chlorochromate, when used in conjunction with 3,5--dimethylpyrazole, is a convenient and useful reagent for the oxidation of allylic alcohols. Saturated primary or secondary alcohols are stable against this reagent [438]:



The oxidation of malic acid by pyridinium chlorochromate is first order with respect to each reactant [439]. The oxidation of the trienol (168) with pyridinium chlorochromate in the presence of py.HCl furnished the trienone (169) in 43% yield [440]:



$$CH_2{=}CH\underset{CH_2}{\overset{}{C}}CH_2CH{=}CH\underset{OH}{\overset{CH_3}{C}}CH_3 \longrightarrow CH_2{=}CH\underset{CH_2}{\overset{}{C}}CH_2\underset{O}{\overset{}{C}}CH{=}\overset{CH_3}{C}CH_3$$

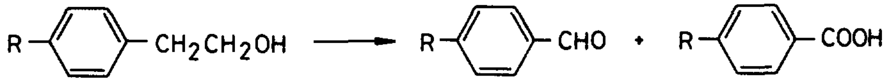
168 169

Ferrocenyl-substituted primary or secondary alcohols can be oxidized to the corresponding carbonyl compounds by oxidizing reagents with fair solubility in organic aprotic solvents, e.g. $[Bu_4N]_2[Cr_2O_7]$, $[Hpy][CrOCl_3]$ and $[Bu_4N][MnO_4]$. Yields are in the range of 50-70% [441]. Primary and secondary alcohols are oxidized to aldehydes or ketones by treatment with solutions of $K_2Cr_2O_7$ (or CrO_3) and Me_3SiCl. The active oxidizing species is suggested to be $Me_3SiOCrO_2Cl$. This reagent is also effective for the selective oxidation of thiols to disulfides and cleavage of oximes to carbonyl compounds [442]. The kinetics of oxidation of propionaldehyde and of isobutyl alcohol by chromic acid was examined in aqueous AcOH. First order dependencies were found for Cr(VI) and the substrates as well [443].

The glycols in the complexes $Mo(NO)_2Cl_2$ diol (diol = 1,2-ethanediol, 2,3-butanediol, 2,4-pentanediol or 1,2-cyclohexanediol) are converted to carbonyl compounds in an intramolecular redox reaction if the complex is heated to 110-230°C [444].

In the oxidation of substituted benzaldehydes by permanganate in acid medium, the rate is increased by electron-donating and decreased by electron-withdrawing groups [445]. The continuous measurement of the dielectric constant was used to determine the kinetics for the $KMnO_4$ oxidation of aldehydes, unsaturated hydrocarbons or phenols [446]. Ultrasonic irradiation facilitates the heterogeneous oxidation of secondary alcohols to ketones with solid $KMnO_4$ in nonpolar organic solvents. Traces of water hinder this effect [447]. Secondary alcohols dissolved in methylene chloride are readily oxidized to the corresponding ketones with hydrated copper permanganate under heterogeneous conditions. Alkenes almost completely inhibit the reaction. When mixtures of saturated and α, β-unsaturated alcohols are treated the unsaturated alcohols are preferentially oxidized. γ, δ-Unsaturated alcohols, however, are not oxidized under these conditions. This suggests, that unsaturated compounds must form organometallic complexes of suitable geometry [448].

Active γ-manganese dioxide oxidizes arylethanols to benzaldehydes and benzoic acids with loss of a carbon atom:



Arylacetaldehydes and arylacetic acids are degraded in a similar way [449]. The kinetics of the oxidation of some hexitols with Mn(III) pyrophosphate were determined [450].

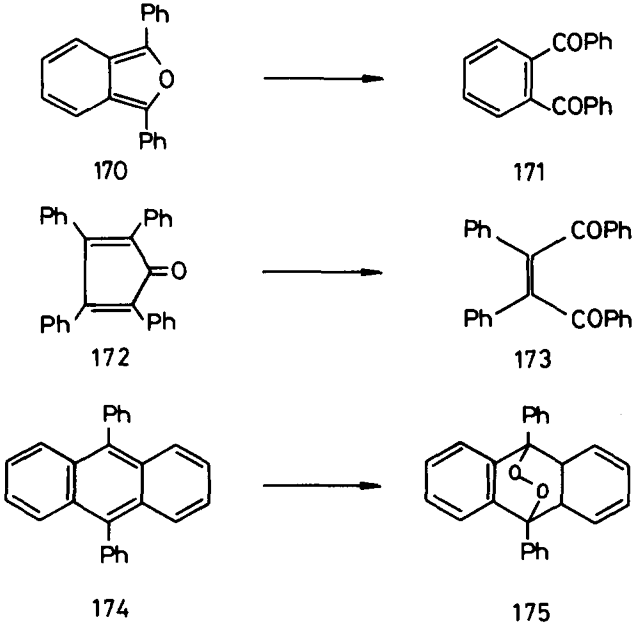
D-Fructose is oxidatively degraded with 80% yield to D-erythrose by $FeCl_3$ under photo-irradiation. C_1-C_3 aldehydes were identified as byproducts. Air had practically no influence on the reaction [451].

The kinetics of the outer-sphere oxidation of L-ascorbic acid (H_2A) by tris-bpy complexes of Os(III), Ru(III) and Ni(III) have been investigated in acidic aqueous media. The inverse acid dependence suggests mechanisms involving H_2A and HA^- pathways [452].

The oxidation of alkylidenebisphenols by Co(III)-coordinated oxygen-containing radicals and by Co(II)-O_2 complexes was examined by ESR [453]. The rate of oxidative cleavage of hydroxibenzoins

PhCH(OH)CR(OH)Ph (R = H,Me,Ph) by $Co(OAc)_3$ in AcOH is first order in $Co(OAc)_3$ and substrate, and inverse first order in Co^{2+}. A mechanism has been proposed [454].

The kinetics of the oxidation of ascorbic acid (H_2A) by $IrCl_6^{2-}$ and $IrBr_6^{2-}$ has been determined in aqueous $LiClO_4$-$HClO_4$ solutions. The reactions are first order with respect to ascorbic acid concentration and first order with respect to Ir(VI) concentration. The acidity dependence is compatible with a dual pathway according which both H_2A and HA^- react with Ir(IV) [455]. Allyl alcohol is oxidized by aqueous $PdCl_2$ to a mixture of β-hydroxypropanal, α-hydroxyacetate, and acrolein. Deuterium-labeling studies show that the first two are formed by the normal olefin oxidation route while acrolein is formed by hydride abstraction from the alcohol carbon [456]. The complex $Pd(PPh_3)_2O_2$ oxidizes (170) and (172) thermally to (171) and (173), respectively. The oxygenation of (174) to (175) requires photochemical conditions [457].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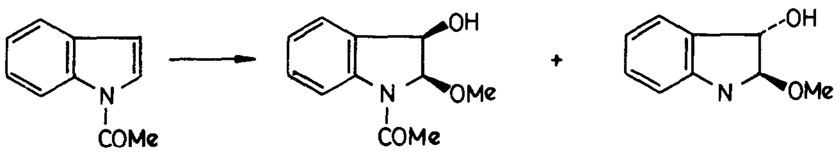
Rate constants and activation parameters were determined for the oxidation of hydroxymethylfurfural by transition metal ions (Cu^{2+}, Fe^{3+}, Ag^+) in acid media [458]. Alcohols are photooxidized to aldehydes by $CuCl_2$ in MeCN solution. Chlorinated aldehydes are formed as byproducts. In the presence of O_2, Cu(I) is reoxidized [459].

d) Oxidation of N-containing Compounds

The kinetics of oxidation of substituted piperidin-4-ols by vanadium(V) has been studied. The primary isotope effect suggests the involvement of the C-H bond on the HO-bearing carbon atom in the rate determining step. A mechanism involving a free radical intermediate has been proposed [460]. The oxidation of triethanolammonium ions with V^{5+} in $HClO_4$ and H_2SO_4 solutions is first order with respect to both reactants and second order with respect to H^+ concentration [461].

2,4-Dinitrobenzoic acid was prepared by oxidizing 2,4-dinitrotoluene with 30-40% $Na_2Cr_2O_7$ in concentrated sulfuric acid at 10-20^{o}C [462]. Pyridinium chlorochromate may be used as a mild and efficient oxidant for the oxidation of 2-nitroalkanols $RCHOHCH(NO_2)R'$ to the corresponding ketones $RCOCH(NO_2)R'$ [463].

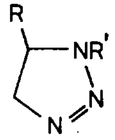
Oxidation of 1-acylindoles (e.g.176) with MoO_5.HMPA in MeOH gave a mixture of cis- and trans-dihydroxyindoline derivatives (177 and 178). If the acylindole is substituted at the 2-position, (179), the corresponding 2-hydroxyindoxyl (180) is formed [464].



176 177 178

179 180

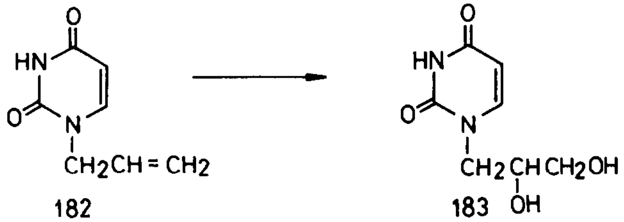
The oxidation of 4-methylpyridine by Mn(IV) is inhibited by Mn(III) [465]. The oxidation kinetics of chloramine-T with alkaline permanganate has been determined [466]. Oxidative dehydrogenation of the aryltriazolines (181) with $KMnO_4$ and quaternary ammonium compounds as phase transfer catalysts gave the corresponding triazoles in 17-94% yield [467]:



181

R = Ph, 2-quinolyl, 2-thienyl
R'= Ph, substituted Ph

Oxidation of 1-allyluracil (182) by $KMnO_4$ gave the dihydroxy derivative (183) [468]:



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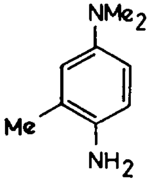
183

The oxidation of tryalkylamines by $Fe(CN)_6^{3-}$ is inhibited by $Fe(CN)_6^{4-}$. Based on kinetic measurements, two rate determining processes were proposed for this oxidation: electron transfer from amine free base (predominant at high pH) and hydrogen transfer from trialkylammonium cation (predominant at lower pH) to Fe(III) [469]. The oxidation of the substituted p-phenylenediamines (184-186) by $Fe(CN)_6^{3-}$ was investigated by the stopped flow method [470].



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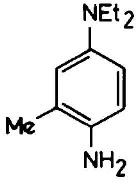

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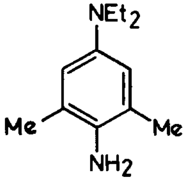

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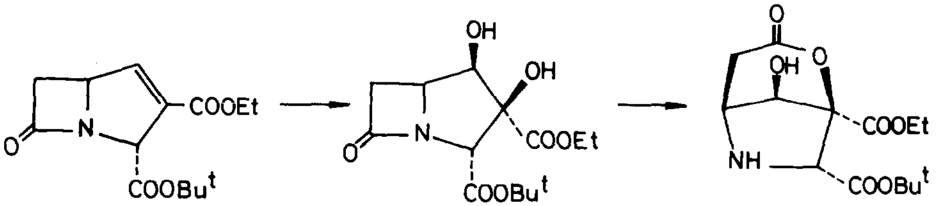
Oxidation of the carbapenem (187) with OsO_4 in py gives the lactone (189). This result implies that cis-hydroxylation of the C=C bond has occured from the endo-face of (187) to yield the cis-diol (188) which then spontaneously rearranges to the product [471].



187 188 189

See also [442].

e) Oxidation of P-, S- or Halogen-containing Compounds

The Mn(IV) porphyrin complexes $[N_3Mn(TPP)]_2O$ and $[ClMn(TPP)(OIPh)]_2O$ oxidize PPh_3 to $OPPh_3$. The stoichiometry of the reaction with the iodosylbenzene complex [472] is the following:

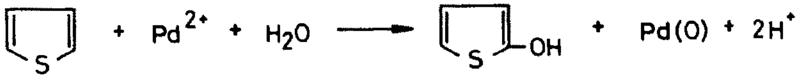
$$[ClMn(TPP)(OPPh)]_2O + 3PPh_3 \longrightarrow 3\ OPPh_3 + 2\ ClMn(TPP) + 2PhI$$

These Mn(IV) complexes also oxidize hydrocarbons to alcohols and ketones at room temperature. The reaction mechanism involves the formation of alkyl radicals via H-abstraction by monomeric oxo complexes followed by electron transfer in the radical cage with subsequent ion pair collapse as the major pathway for alcohol formation [473]. Triphenylphosphine is oxidized to triphenylphosphine oxide by μ-oxo-bis phthalocyaninatoiron(III) $[PcFe]_2O)$ in the presence of pyridine [474]:

$$[PcFe]_2O + PPh_3 \xrightarrow{py} [2\ PcFe(py)_2] + OPPh_3$$

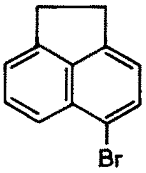
The kinetics of oxidative decarboxylation of L-cysteine by permanganate in aqueous H_2SO_4 is first order in permanganate and cystein [475]. Sulfides and sulfoxides were easily oxidized to the corresponding sulfones in 81-98% yields by $KMnO_4$ in conjuction with a phase transfer agent [476]. The oxidation of L-cysteine, mercaptoacetic acid and β-mercapto ethylamine with 12-tungstocobaltate(III) was investigated. One mole of each of the thiols is oxidized to the corresponding disulfide by one mole of 12-tungstocobaltate(III). No evidence was found for the formation of an intermediate complex of significat stability [447]. Glutathione (GSH) is oxidized by

$Co(III)O_4W_{12}O_{36}^{5-}$ to the corresponding disulfide (GSSG). The rate determining step is the one-electron oxidation of GS^- by Co(III). Since no spectroscopic evidence could be obtained for a complex formation between these two species the oxidation has most probably an outer-sphere mechanism [478]. The kinetics of the hydroxylation of thiophene by Pd(II) in water solution was studied:



2-thienyl-Pd has been proposed as intermediate of the reaction [479].

Oxidation of primary alkyl bromides by $K_2Cr_2O_7$ or K_2CrO_4 in the presence of dicyclohexyl-18-crown-6 in DMF gave the corresponding aldehydes in 20-50% yield and (as byproducts) alcohols [480]. The oxidation of 5-bromo-acenaphtene (190) with $Na_2Cr_2O_7$ in AcOH gives (191) and (192). The two compounds were formed partly over a common intermediate but (192) could also be formed from (191) [481].



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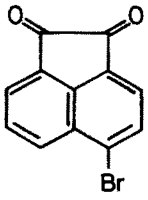

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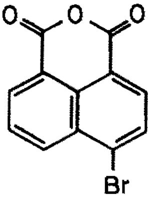

192

The kinetics of the oxidation of substituted phenacyl bromides with $H_2Cr_2O_7$ in 90% AcOH has been investigated. The data conform to a mechanism involving an enol intermediate. Mn(II) ions or complexing agents like succinic acid or pyridine decrease the rate [482].

See also [425, 442].

7. Electrooxidation

The iron(III) porphyrin complex $Fe(TPP)F_2^-$ catalyzes the electrochemical oxidation of cyclohexene to cyclohexanone, 2-cyclohexenol and cyclohexene oxide as principal products [483].

V. Reviews

Organometallics in synthesis. 270 refs. [484].

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Hydroformylation of unsaturated compounds. 64 refs. [501].

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Production of amino acids by hydroformylation of aldehydes. 6 refs. [503].

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Asymmetric hydrogenation. 26 refs. [505].

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Electrocatalysis on transition metal chelates. 89 refs. [525].

List of Abbreviations

bpy = 2,2'-bipyridine
COD = 1,5-cyclooctadiene
Cp = η^5-cyclopentadienyl
Cy = cyclohexyl
(-)-DIOP = see Fig.(11)
(+)-DIOP = see Fig.(33a)
dmgH = dimethylglyoxime
dppe = $Ph_2PCH_2CH_2PPh_2$
HD = 1,5-hexadiene
HMPA = hexamethylphosphoric triamide
NBD = norbornadiene
nmen = neomenthyl
men = menthyl
o.y. = optical yield
phen = 1,10-phenanthroline
py = pyridine
salen = N,N'-bis(salicylidene)-ethylenediamino
st = stearate, $nC_{17}H_{35}COO$
tpm = triphenylphosphine m-monosulfonate, $PPh_2(C_6H_4SO_3Na)$
TPP = mesotetraphenylphorphyrin dianion
triphos = $MeC(CH_2PPh_2)_3$

Metal Index

The numbers give those references which deal with the use of the metal as reagent or catalyst.

Ti 232, 234, 359, 360, 369, 401

Ir 3, 67, 81, 90, 92, 102, 128, 129, 162, 184, 200, 219-221, 223, 226, 227, 276, 455

Ni 91, 114, 120, 206, 259, 288, 296, 299, 314, 324, 396, 406, 452

Pd 98, 120, 130-138, 161, 171, 192, 195-197, 201, 239, 240, 252, 277, 278, 280, 281, 332, 337, 343, 348, 357, 358, 397-399, 426-431, 456, 457, 479, 493-495, 521, 522

Pt 20, 40-45, 57, 103-105, 137-139, 172, 173, 182, 241-244, 252, 265, 282, 351, 495

Cu 175, 229, 266, 274, 278, 279, 281, 283, 284, 288, 293, 297, 300-302, 309-314, 316, 320, 324, 332-334, 343, 344, 346, 399, 400, 406, 407, 432, 448, 458, 459, 523, 524

Ag 351, 458

Transition metals, general 91, 183, 204, 255, 256

References

1 K.F.Purcell, J.Organometal.Chem. 252 (1983) 181

2 P.Pelikán, S.Weerarathna and M.Hronec, J.Mol.Catal. 19 (1983) 17

3 J.P.Collman, J.I.Brauman, G.Tustin and G.S.Wann, J.Am.Chem. Soc. 105 (1983) 3913

4 G.N.Petrova, O.N.Efimov and V.V.Strelets, Izv.Akad.Nauk SSSR, Ser.Khim. (1982) 2608

5 B.D.Dombek, J.Organometal.Chem. 250 (1983) 467

6 B.K.Warren and B.D.Dombek, J.Catal. 79 (1983) 334

7 J.F.Knifton, J.C.S.Chem.Commun. (1983) 729

8 R.Whyman, J.C.S.Chem.Commun. (1983) 1439

9 R.Pierantozzi, E.G.Valagene, A.F.Nordquist and P.N.Dyer, J.Mol. Catal. 21 (1983) 189

10 M.G.Katsnel'son, V.B.Del'nik, Sh.S.Kagna, V.V.Kashina and E.I.Leenson, Neftekhimiya 22 (1982) 683

11 Yu.M.Levin, Zh.Prikl.Khim. (Leningrad) 56 (1983) 99; CA 98 (1983) 217917

12 V.B.Del'nik and M.G.Katsnel'son, Neftepererab.Neftekhim. Moscow (1983) 6 23; CA 99 (1983) 89853

13 Y.Matsui and M.Orchin, J.Organometal.Chem. 246 (1983) 57

14 B.Falk and B.Fell, J.Mol.Catal., 18 (1983) 127

15 P.Pino, F.Oldani and G.Consiglio, J.Organometal.Chem. 250 (1983) 491

16 Yu.T.Vigranenko, V.A.Rybakov, R.B.Borisov, B.G.Sokolov and M.V.Khokhlova, Zh.Prikl.Khim. Leningrad 56 (1983) 1619; CA 99 (1983) 175157

17 J.D.Fellmann, P.E.Garrou, H.P.Withers, D.Seyferth and D.D. Traficante Organometallics 2 (1983) 818

18 Yu.B.Kagan, O.L.Butkova, G.A.Korneeva, M.V.Shishkina, L.I. Zvezdkina and A.N.Bashkirov, Neftekhimiya 23 (1983) 77; CA 99 (1983) 5143

19 A.D.Harley, G.J.Guskey and G.L.Geoffroy, Organometallics 2 (1983) 53

20 W.Zhai, D.Li, Y.Ma and Z.Zhao, Youji Huaxue (1983) 180; CA 99 (1983) 114918

21 C.Mahe, H.Patin, J.-Y.Le Marouille and A.Benoit, Organometallics 2 (1983) 1051

22 M.J.Mirbach, N.Topalsavoglou, T.N.Phu, M.F.Mirbach and A.Saus, Chem.Ber. 116 (1983) 1422

23 P.Salvadori, G.Vitulli, A.Raffaelli and R.Lazzaroni, J.Organometal.Chem. 258 (1983) 351

24 R.Lazzaroni, S.Pucci, S.Bertozzi and D.Pini, J.Organometal. Chem. 247 (1983) C56

25 H.L.Pelt, L.A.Gerritsen, G.Van der Lee and J.J.F.Scholten, Stud.Surf.Sci.Catal. 16 (1983) 369; CA 99 (1983) 94360

26 R.Grigg, G.J.Reimer and A.R.Wade, J.C.S.Perkin Trans.I (1983) 1929

27 A.G.Abatjoglou, D.R.Bryant and L.C.d'Esposito, J.Mol.Catal. 18 (1983) 381

28 W.Pan, J.Liu, S.Li, Y.Xia and D.Liu, Gaodeng Xuexiao Huaxue Xuebao (1982) 107; CA 98 (1983) 197467

29 M.Matsumoto and M.Tamura, J.Mol.Catal. 19 (1983) 365

30 A.M.Trzeciak and J.J.Ziółkowski, J.Mol.Catal. 19 (1983) 41

31 P.W.N.M. van Leeuwen and C.F.Roobeek, J.Organometal.Chem. 258 (1983) 343

32 W.R.Jackson and C.G.Lovel, Aust.J.Chem. 35 (1982) 2069

33 C.U.Pittman and W.D.Honnick, Chem.Ind. (Dekker) 5 (1981) 353; CA 99 (1983) 37987

34 J.D.Unruh, J.R.Christenson, O.R.Hughes and D.A.Young, Chem. Ind. (Dekker) 5 (1981) 309; CA 98 (1983) 197403

35 S.Gladiali, G.Faedda, M.Marchetti and C.Botteghi, J.Organometal.Chem. 244 (1983) 289

36 R.T.Smith, R.K.Ungar, L.J.Sanderson and M.C.Baird, Organometallics 2 (1983) 1138

37 R.A.Jones, T.C.Wright, J.L.Atwood and W.E.Hunter, Organometallics 2 (1983) 470

38 P.Kalck, J.-M.Frances, P.-M.Pfister, T.G.Southern and A.Thorez, J.C.S.Chem.Commun. (1983) 510

39 A.Saus, T.N.Phu, M.J.Mirbach and M.F.Mirbach, J.Mol.Catal. 18 (1983) 117

40 G.K.Anderson, C.Billard, H.C.Clark, J.A.Davies and C.S.Wong, Inorg. Chem. 22 (1983) 439

41 G.K.Anderson, H.C.Clark and J.A.Davies, Inorg.Chem. 22 (1983) 427

42 G.K.Anderson, H.C.Clark and J.A.Davies, Inorg.Chem. 22 (1983) 434

43 G.Cavinato and L.Toniolo, J.Organometal.Chem. 241 (1983) 275

44 G.Consiglio, P.Pino, L.I.Flowers and C.U.Pittman, J.C.S.Chem. Commun.(1983) 612

45 C.U.Pittman, G.M.Wilemon, Q.Y.Ng and L.I.Flowers, Polym.Prep. 22 (1981) 153; CA 98 (1983) 88787

46 M.Bianchi, G.Menchi, P.Frediani, U.Matteoli and F.Piacenti, J.Organometal.Chem. 247 (1983) 89

47 R.A.Sánchez-Delgado, A.Andriollo and N.Valencia, J.C.S.Chem. Commun. (1983) 444

48 C.De-An and C.U.Pittman, J.Mol.Catal. 21 (1983) 405

49 H.P.Withers and D.Seyferth, Inorg.Chem. 22 (1983) 2931

50 Y.Wang, N.Wu, A.Zhang, H.Fu, Y.Luo and Z.Yang, Cuihua Xuebao 4 (1983) 154; CA 99 (1983) 77530

51 Y.Luo, H.Fu, Y.Wang, L.Wu and A.Zhang, China-Jpn.-U.S. Symp. Heterog.Catal.Relat.Energy Probl. (1982) A13C; CA 99 (1983) 182164

52 G.Su, Y.Chen, S.Yang, S.Luo, W.Xie and Z.Yang, China-Jpn-U.S.Symp.Heterog.Catal.Relat.Energy Probl. (1982) B07C; CA 99 (1983) 212117

53 M.E.Ford and J.E.Premecz, J.Mol.Catal. 19 (1983) 99

54 M.Ding and J.K.Stille, Macromolecules 16 (1983) 839

55 J.P.Collman, J.A.Belmont and J.I.Brauman, J.Am.Chem.Soc. 105 (1983) 7288

56 F.Farzaneh and T.Pinnavaia, Inorg.Chem. 22 (1983) 2216

57 J.K.Stille and G.Parrinello, J.Mol.Catal. 21 (1983) 203

58 A.S.C.Chan, W.E.Carrol and D.E.Willis, J.Mol.Catal. 19 (1983) 377

59 P.Hong, T.Mise and H.Yamazaki, Chem.Lett. (1982) 361

60 H.Yamazaki and P.Hong, J.Mol.Catal. 21 (1983) 133

61 P.B.Francoisse and F.C.Thyrlon, Ind.Eng.Chem.Prod.Res.Dev. 22 (1983) 542

62 M.Röper and H.Loevenich, J.Organometal.Chem. 255 (1983) 95

63 G.Doyle, J.Mol.Catal. 18 (1983) 251

64 Y.Uchida, Kenkyu Hokoku - Asahi Garasu Kogyo Gijutsu Shoreikai 40 (1982) 49; CA 99 (1983) 111360

65 M.Hidai, M.Orisaku, M.Ue, Y.Koyasu, T.Kodama and Y.Uchida, Organometallics 2 (1983) 292

66 P.Andrianary, G.Jenner and A.Kiennemann, J.Organometal.Chem. 252 (1983) 209

67 G.R.Steinmetz and T.H.Larkins, Organometallics 2 (1983) 1879

68 M.Novotny and I.L.Mador, Chem.Ind. (Dekker) 5 (1981) 249; CA 98 (1983) 182380

69 H.Kheradmand, G.Jenner, A.Kiennemann and A.Deluzarche, Chem. Lett. (1982) 395

70 H.Kheradmand, A.Kiennemann and G.Jenner, J.Organometal.Chem. 251 (1983) 339

71 G.Jenner, H.Kheradmand, A.Kiennemann and A.Deluzarche, J.Mol. Catal., 18 (1983) 61

72 P.A.Belmonte, F.G.N.Cloke and R.R.Schrock, J.Am.Chem.Soc. 105 (1983) 2643

73 K.Kropp, V.Skibbe, G.Erker and C.Krüger, J.Am.Chem.Soc. 105 (1983) 3353

74 C.Lapinte and D.Astruc, J.C.S.Chem.Commun. (1983) 430

75 M.A.Drezdzon and D.F.Shriver, J.Mol.Catal. 21 (1983) 81

76 B.D.Dombek and A.M.Harrison, J.Am.Chem.Soc. 105 (1983) 2485

77 Y.Matsui and M.Orchin, J.Organometal.Chem. 244 (1983) 369

78 A.Sisak, F.Ungváry and L.Markó, Organometallics 2 (1983) 1244

79 F.Ungváry, Acta Chim.Acad.Sci.Hung. 111(1982) 117; CA 98 (1983) 198410

80 F.Ungváry and L.Markó, Organometallics 2 (1983) 1608

81 T.Hayashi, M.Tanaka, I.Ogata, T.Kodama, T.Takahashi, Y.Uchida and T.Uchida, Bull.Chem.Soc.Jpn. 56 (1983) 1780

82 M.Lourdichi, R.Pince, F.Dahan and R.Mathieu, Organometallics 2 (1983) 1417

83 J.T.Martin and M.C.Baird, Organometallics 2 (1983) 1073

84 M.Iwamoto, H.Kusano and S.Kagawa, Chem.Lett. (1983) 1483

85 K.Tanaka, M.Morimoto and T.Tanaka, Chem.Lett. (1983) 901

86 M.Pavlik, M.F.Hoq and R.E.Shepherd, J.C.S.Chem.Commun. (1983) 1467

87 P.Yarrow, H.Cohen, C.Ungermann, D.Vandenberg, P.C.Ford and R.G.Rinker, J.Mol.Catal. 22 (1983) 239

88 F.Wada, M.Shimuta, T.Goto, T.Ikeda, K.Kikukawa and T.Matsuda, Chem.Lett. (1983) 1837

89 J.M.Basset, B.Besson, A.Choplin and A.Theolier, Philos.Trans. R.Soc.London, Ser.A 308 (1982) 115; CA 98 (1983) 96375

90 R.Ganzerla, F.Pinna, M.Lenarda and M.Graziani, J.Organometal. Chem., 244 (1983) 183

91 D.C.Elliott and L.J.Sealock, Ind.Eng.Chem.,Prod.Res.Dev. 22 (1983) 426

92 J.Kaspar, R.Spogliarich, A.Cernogoraz and M.Graziani, J.Organometal.Chem. 255 (1983) 371

93 T.Okano and T.Yoshida, Yuki Gosei Kagaku Kyokaishi 41 (1983) 359; CA 99 (1983) 53950

94 M.A.Radhi, G.Pályi and L.Markó, J.Mol.Catal. 22 (1983) 195

95 E.Alessio, G.Zassinovich and G.Mestroni, J.Mol.Catal. 18 (1983) 113

96 Y.Watanabe, Y.Tsuji, T.Ohsumi and R.Takeuchi, Tetrahedron Lett. 24 (1983) 4121

97 K.Kaneda, T.Imanaka and S.Teranishi, Chem.Lett. (1983) 1465

98 V.P.Baillargeon and J.K.Stille, J.Am.Chem.Soc. 105 (1983) 7175

99 D.J.Darensbourg, C.Ovalles and M.Pala, J.Am.Chem.Soc. 105 (1983) 5937

100 B.Kim and S.L.Regen, Tetrahedron Lett. 24 (1983) 689

101 W.J.S.Lockley, Synth.Appl.Isot.Labeled Compd.,Proc.Int.Symp. (1982) 427; CA 98 (1983) 215266

102 B.J.Fisher and R.Eisenberg, Organometallics 2 (1983) 764

103 A.F.Shestakov and S.M.Vinogradova, Koord.Khim. 9 (1983) 248

104 E.A.Karakhanov, A.G.Dedov, A.S.Loktev, L.V.Popov, P.A.Sharbatyan and I.V.Arkhangel'skii, Khim.Ceterotsikl.Soedin. 1983 754; CA 99 (1983) 87587

105 A.G.Dedov, T.Yu.Filippova, E.B.Neimerovets, L.V.Popov, I.P. Stephanova and E.A.Karakhanov, Khim.Geterosikl.Soedin. (1983) 912; CA 99 (1983) 122210

106 H.Inoue and M.Sato, J.C.S.Chem.Commun. (1983) 983

107 A.R.Brodskii, N.F.Noskova, D.V.Sokol'skii and A.S.Khlystov, Dokl.Akad.Nauk SSSR 286 (1983) 1430

108 S.R.Patil, D.N.Sen and R.V.Chaudhari, J.Mol.Catal. 19 (1983) 233

109 C.E.Rodgers, W.R.Cullen and B.R.James, Can.J.Chem. 61 (1983) 1314

110 L.M.Wilkes, J.H.Nelson, L.B.McCusker, K.Seff and F.Mathey, Inorg.Chem. 22 (1983) 2476

111 L.Vigh, F.Joó, P.R.van Hasselt and P.J.C.Kuiper, J.Mol. Catal. 22 (1983) 15

112 Y.Doi, S.Tamura and K.Koshizuka, J.Mol.Catal. 19 (1983) 213

113 J.R.Budge, J.P.Scott and B.C.Cates, J.C.S.Chem.Commun. (1983) 342

114 P.Moggi, G.Albanesi, G.Predieri and E.Sappa, J.Organometal. Chem. 252 (1983) C89

115 M.B.Mooiman and J.M.Pratt, J.C.S.Chem.Commun. (1981) 33

116 M.B.Mooiman, J.M.Pratt and E.H.R.von Barsewisch, S.Afr.J. Chem. 35 (1982) 175

117 J.Halpern, Inorg.Chim.Acta 77 (1983) L105

118 R.Lykvist and R.Larsson, J.Mol.Catal. 19 (1983) 1

119 H.Alper and J.Heveling, J.C.S.Chem.Commun. (1983) 365

120 E.J.Ucciani and R.Stern, Zesz.Probl.Postepow Nauk Roln. 211 (1981) 221; CA 98 (1983) 214363

121 J.G.Wadkar and R.V.Chaudhari, J.Mol.Catal. 22 (1983) 103

122 Ya.L.Goldfarb, E.I.Klabunovskii, A.A.Dudinov, L.N.Sukhobok, V.A.Pavlov, B.D.Polkovniskov and V.P.Litvinov, Izv.Akad.Nauk SSSR, Ser.Khim. (1983) 1880

123 W.R.Cullen, T.J.Kim, F.W.B.Eistein and T.Jones, Organometallics 2 (1983) 714

124 R.Raythatha and T.J.Pinnavaia, J.Catal. 80 (1983) 47

125 P.E.Kreter and D.W.Meek, Inorg.Chem. 22 (1983) 319

126 M.D.Fryzuk, Can.J.Chem. 61 (1983) 1347

127 J.Blum, I.Amer, A.Zoran and Y.Sasson, Tetrahedron Lett. 24 (1983) 4139

128 R.H.Crabtree and M.W.Davis, Organometallics 2 (1983) 681

129 G.Stork and D.E.Kahne, J.Am.Chem.Soc. 105 (1983) 1072

130 E.E.Nifant'ev, T.S.Kukhareva, M.Yu.Antipin, Yu.T.Struchkov and E.I.Klabunovsky, Tetrahedron 39 (1983) 797

131 E.E.Nifant'ev, T.S.Kukhareva, M.Yu.Antipin and Yu.T.Struchkov, Zh.Obshch.Khim. 52 (1982) 2736

132 A.S.Berenblyum, S.L.Mund, L.G.Danilova, T.P.Goranskaya, A.S. Malinovskii and I.I.Moiseev, Izv.Akad.Nauk SSSR, Ser.Khim. (1983) 1926

133 P.Feng and S.Shen, Zhongguo Kexue Jishu Daxue Xuebao 13 (1983) 188; CA 99 (1983) 201132

134 H.Liu, Cuihua Xuebao 3 (1982) 315; CA 98 (1983) 125157

135 Z.Feng and H.Liu, Caofenzi Tongxun (1982) 261; CA 98 (1983) 71427

136 Y.Chen, J.Liu, Y.Lin, C.Xiao and C.Mai, Wuhan Daxue Xuebao, Ziran Kexueban (3)(1982) 29; CA 98 (1983) 82741

137 D.H.Goldsworthy, F.R.Hartley and S.G.Murray, J.Mol.Catal. 19 (1983) 257

138 D.H.Goldsworthy, F.R.Hartley and S.G.Murray, J.Mol.Catal. 19 (1983) 269

139 R.Rumin, J.Organometal.Chem. 247 (1983) 351

140 L.C.Nindakova, V.A.Pavlov, F.K.Shmidt and E.I.Klabunovskii, Izv.Akad.Nauk SSSR, Ser.Khim. (1982) 2094

141 F.K.Shmidt, L.O.Nindakova, V.V.Saraev and E.I.Klabunovskii, Geterog.Katal.,Mater.Vses.Konf.Mekh.Katal.Reakts.,3rd 1981 (1982) 169; CA 98 (1983) 222606

142 P.Le Maux and G.Simonneaux, J.Organometal.Chem. 252 (1983) C60

143 M.Bianchi, U.Matteoli, P.Frediani, G.Menchi, F.Piacenti, C.Botteghi and M.Marchetti, J.Organometal.Chem. 252 (1983) 317

144 C.R.Landis and J.Halpern, J.Organometal.Chem. 250 (1983) 485

145 J.M.Brown, L.R.Canning, A.J.Downs and A.M.Forster, J.Organometal.Chem. 255 (1983) 103

146 J.M.Brown, P.A.Chaloner and G.A.Morris, J.C.S.Chem.Commun. (1983) 664

147 H.Brunner, B.Schönhammer, B.Schönhammer and C.Steinberger, Chem.Ber. 116 (1983) 3529

148 V.A.Pavlov and E.I.Klabunivskii, Dokl.Akad.Nauk SSSR 269 (1983) 856

149 C.Cativiela, J.A.Mayoral, E.Melendez, R.Uson, L.A.Oro and M.T.Pinillos, React.Kinet.Catal.Lett. 21 (1982) 173; CA 98 (1983) 198672

150 J.D.Oliver and D.P.Riley, Organometallics 2 (1983) 1032

151 D.L.Allen, V.C.Gibson, M.L.H.Green, J.F.Skinner, J.Bashkin and P.D.Grebenik, J.C.S.Chem.Commun. (1983) 895

152 J.Bakos, B.Heil and L.Markó, J.Organometal.Chem. 253 (1983) 249; 255 (1983) C19

153 P.J.Irrure and R.A.Bosch, Affinidad 39 (1982) 224; CA 98 (1983) 54143

154 P.J.Irrurre and R.A.Bosch, Afinidad 39 (1982) 490; CA 98 (1983) 179592

155 A.Uehara, T.Kubota and R.Tsuchiya, Chem.Lett. (1983) 441

156 E.Cesarotti, A.Chiesa, G.Ciani and A.Sironi, J.Organometal. Chem. 251 (1983) 79

157 M.Yatagai, M.Zama, T.Yamagishi and M.Hida, Chem.Lett (1983) 1203

158 R.Mutin, W.Abboud, J.M.Basset and D.Sinou, Polyhedron 2 (1983) 539

159 V.A.Pavlov, N.I.Spitsyna and E.I.Klabunovskii, Izv.Akad. Nauk SSSR, Ser.Khim. (1982) 2838

160 V.A.Pavlov, N.I.Spotsyna and E.I.Klabunovskii, Izv.Akad. Nauk SSSR, Ser.Khim. (1983) 1653

161 E.E.Nifant'ev, A.T.Teleshov and M.P.Koroteev, Zh.Obshch. Khim. 53 (1983) 1640

162 L.A.Oro, J.A.Cabeza, C.Cativiela, M.D.Diaz de Villegas and R.Meléndez, J.C.S.Chem.Commun. (1983) 1383

163 P.Le Maux, R.Dabard and G.Simonneaux, J.Organometal.Chem. 241 (1983) 37

164 R.F.Gerlach, D.N.Duffy and M.D.Curtis, Organometallics 2 (1983) 1172

165 M.McKenna, L.L.Wright, D.J.Miller, L.Tanner, R.C.Haltiwagner and M.Rakowski DuBois, J.Am.Chem.Soc. 105 (1983) 5329

166 C.Sun, Q.Huang, S.Niu and S.Li, Gaofenzi Tongxun 1982 248; CA 98 1983 22867

167 L.A.Hughes, L.N.Hui and G.N.Schrauzer, Organometallics 2 (1983) 486

168 R.R.Burch, A.J.Schusterman, E.L.Muetterties, R.G.Teller and J.M.Williams, J.Am.Chem.Soc. 105 (1983) 3546

169 M.Airoldi, G.Deganello, G.Dia and G.Gennaro, Inorg.Chim.Acta 68 (1983) 179

170 J.M.G.Figueroa and J.M.Winterbottom, J.Chem.Technol.Biotechnol. 32 (1982) 857; CA 98 (1983) 88633

171 A.Sisak, F.Ungváry and G.Kiss, J.Mol.Catal. 18 (1983) 223

172 A.Fusi, R.Ugo, R.Psaro, P.Braunstein and J.Dehand, Philos. Trans.R.Soc.London Ser.A 308 (1982) 125; CA 98 (1983) 125159

173 R.Bertani, G.Garturan and A.Scrivanti, Angew.Chem. 95 (1983) 241

174 L.N.Lewis and K.G.Caulton, J.Organometal.Chem. 252 (1983) 57

175 X.Liu, N.Liu and Y.Men, Lanzhou Daxue Xuebao, Ziran Kexueban 19 (1983) 81; CA (1983) 37824

176 R.Wilczynski, W.A.Fordyce and J.Halpern, J.Am.Chem.Soc. 105 (1983) 2066

177 V.E.Zadov, A.V.Finkel'shtein and A.A.Vaisburd, Deposited Doc. (1982) VINITI 3505-82; CA 99 (1983) 104574

178 C.R.Landis and J.Halpern, Organometallics 2 (1983) 840

179 D.Pieta, A.M.Trzeciak and J.J.Ziólkowski, J.Mol.Catal. 18 (1983) 193

180 A.F.Borowski, Transition Met.Chem. 8 (1983) 266

181 K.R.Januszkiewicz and H.Alper, Organometallics 2 (1983) 1054

182 Y.Z.Zhou, D.X.Wang and Y.Y.Jiang, J.Mol.Catal. 19 (1983) 283

183 G.A.Cremer, T.Vermeulen and R.H.Fish, Report LBL-14216 (1982); CA 98 (1983) 75124

184 R.K.Sharma and G.Moffett, Prepr.Pap. - Am.Chem.Soc.,Div.Fuel Chem. 27 (1982) 2 11; CA 99 (1983) 161135

185 F.Fournier, J.Berthelot and Y.L.Pascal, Can.J.Chem. 61 (1983) 2121

186 L.Markó and J.Palágyi, Transition Met.Chem. 8 (1983) 207

187 R.A.Sanchez-Delgado, A.Andriollo, K.Doppert, C.Ramirez and N.Valencia, Acta.Cient.Venez. 33 (1982) 23 ; CA 98 (1983) 34189

188 K.A.Alekseeva, R.B.Borisov and M.V.Khokhlova, Neftepererab. Neftekhim. (Moscow) (1983) 39; CA 98 (1983) 125362

189 S.Tőrös, L.Kollár, B.Heil and L.Markó, J.Organometal.Chem. 253 (1983) 375

190 L.Kollár and S.Tőrös, Magy.Kém.Lapja 38 (1983) 223; CA 99 (1983) 122721

191 S.Tőrös, L.Kollár, B.Heil and L.Markó, J.Organometal.Chem. 255 (1983) 377

192 Y.Z.Zhou and Y.Y.Jiang, J.Organometal.Chem. 251 (1983) 31

193 S.Tyrlik, M.Kwiecinski, A.Rockenbauer and M.Györ, J.Coord. Chem. 11 (1982) 205

194 K.Januszkiewicz and H.Alper, J.Mol.Catal. 19 (1983) 139

195 S.Bhattacharya, P.Khandual and C.R.Saha, Chem.Ind. London (1982) 600

196 A.V.Bulatov, M.L.Khidekel, A.N.Egorochkin, M.V.Panicheva and P.G.Sennikov, Transition Met.Chem. 8 (1983) 289

197 Y.J.Li and Y.Y.Jiang, J.Mol.Catal. 19 (1983) 277

198 R.M.Laine, J.Mol.Catal. 21 (1983) 119

199 J.C.Woo and C.S.Chin, Bull.Korean Chem.Soc. 4 (1983) 169; CA 99 (1983) 211960

200 C.J.Moon and C.S.Chin, Bull.Korean Chem.Soc. 4 (1983) 180; CA 99 (1983) 211961

201 H.Eckert, G.Fabry, Y.Kiesel, G.Raudaschl and C.Seidel, Angew.Chem. 95 (1983) 894

202 S.G.Hardin and D.W,Turney, Aust.J.Chem. 35 (1982) 1599

203 M.Rakowski DuBois, J.Am.Chem.Soc. 105 (1983) 3710

204 D.R.Anton and R.H.Crabtree, Organometallics 2 (1983) 855

205 D.C.Roe, J.Am.Chem.Soc. 105 (1983) 7770

206 M.Castiglioni, R.Giordano and E.Sappa, J.Organometal.Chem. 258 (1983) 217

207 T.Yamamura, G.Christou and R.H.Holm, Inorg.Chem. 22 (1983) 939

208 S.Shinoda, T.Kojima and Y.Saito, J.Mol.Catal. 18 (1983) 99

209 K.Yoshinaga, T.Kito and K.Ohkubo, Nippon Kagaku Kaishi (1982) 1838; CA 98 (1983) 52797

210 R.Irie, X.Li and Y.Saito, J.Mol.Catal. 18 (1983) 263

211 E.Delgado-Lieta, M.A.Luke, R.F.Jones and D.J.Cole-Hamilton, Polyhedron 1 (1982) 839

212 D.Baudry, M.Ephritikhine, H.Felkin and R.Holmes-Smith, J.C. S.Chem.Commun. (1983) 788

213 Y.Lin and X.Lu, J.Organometal.Chem. 251 (1983) 321

214 Y.Ishii, K.Osakada, T.Ikariya, M.Saburi and S.Yoshikawa, Tetrahedron Lett. 24 (1983) 2677

215 Y.Matsui, T.E.Nalesnik and M.Orchin, J.Mol.Catal. 19 (1983) 303

216 D.Beaupere, L.Nadjo, R.Uzan and P.Bauer, J.Mol.Catal. 18 (1983) 73

217 D.Beaupere, L.Nadjo, R.Uzan and P.Bauer, J.Mol.Catal. 20 (1983) 185

218 D.Beaupere, L.Nadjo, R.Uzan and P.Bauer, J.Mol.Catal. 20 (1983) 195

219 J.Azran, O.Buchman, G.Höhne, H.Schwarz and J.Blum, J.Mol. Catal. 18 (1983) 105

220 S.M.Pillai, S.Vancheesan, J.Rajaram and J.C.Kuriacose, J.Mol.Catal. 20 (1983) 169

221 S.M.Pillai, S.Vancheesan, J.Rajaram and J.C.Kuriakose, Proc.Catsympo 80, Natl.Catal.Symp.,5th 1980, 112; CA 99 (1983) 121588

222 L.A.Oro, M.P.Lamata and M.Valderrame, Transition Met.Chem. 8 (1983) 48

223 F.Vinzi, G.Zassinovich and G.Mestroni, J.Mol.Catal. 18 (1983) 359

224 G.Zassinovich and F.Grisoni, J.Organometal.Chem. 247 (1983) C24

225 K.Yoshinaga, T.Kito and K.Ohkubo, Bull.Chem.Soc.Jpn. 56 (1983) 1786

226 G.Mestroni, G.Zassinovich, C. del Bianco and A.Camus, J.Mol. Catal., 18 (1983) 33

227 Y.Migron, J.Blum and Y.Sasson, J.Mol.Catal. 22 (1983) 187

228 M.Massoui, D.Beaupere, L.Nadjo and R.Uzan, J.Organometal. Chem. 259 (1983) 345

229 C.Bianchini, C.A.Chilardi, A.Meli, S.Midollini and A.Orlandini, J.Organometal.Chem. 248 (1983) C13

230 G.P.Boldrini, G.Cainelli and A.Umani-Ronchi, J.Organometal. Chem. 243 (1983) 195

231 J.-B-NGuini Effa , B.Djebailli, J.Lieto and J.-P.Aune, J.C.S.Chem.Commun. (1983) 408

232 V.A.Kopeikin, V.V.Kopeikin, G.S.Mironov,Yu.Yu.Musabekov and V.A.Ustinov, Zh.Org.Khim. 19 (1983) 1555; CA 99 (1983) 157961

233 N.Rybakova, L.N.Kiseleva and I.V.Laputina, Izv.Akad.Nauk SSSR, Ser.Khim. (1983) 863

234 J.George and S.Chandrasekaran, Synth.Commun. 13 (1983) 495

235 N.Oguni, S.Shimazu and A.Nakamura, J.Mol.Catal. 22 (1983) 1

236 Y.Nambu, M.Kijima, T.Endo and M.Okawara, J.Mol.Catal. 18 (1983) 141

237 R.Steinberger, M.Michman, H.Schwarz and G.Höhne, J.Organometal.Chem. 244 (1983) 283

238 A.Fischli, Helv.Chim.Acta 65 (1982) 2697

239 N.Suzuki, T.Tsukanaka, T.Nomoto, Y.Ayaguchi and Y.Izawa, J.C.S.Chem.Commun. (1983) 515

240 E.Keinan and N.Creenspoon, J.Org.Chem. 48 (1983) 3545

241 V.V.Zamashchikov, E.S.Rudakov, S.A.Mitchenko and S.L.Litvinenko, Mekh.Katal.Reakts.,Mater.Vses.Konf., 3rd 2 (1982) 70; CA 99 (1983) 37837

242 V.V.Zamashchikov, E.S.Rudakov and S.A.Mitchenko, React.Kinet. Katal.Lett. 21 (1982) 157

243 V.V.Zamashchikov, E.S.Rudakov and S.A.Mitchenko, Zh.Obsch. Khim. 52 (1982) 2536

244 S.Bhaduri and K.R.Sharma, J.C.S.Chem.Commun. (1983) 1412

245 D.Wang and T.H.Chan, Tetrahedron Lett. 24 (1983) 1573

246 H.Brunner, G.Riepl and H.Weitzer, Angew.Chem. 95 (1983) 326

247 V.S.Lenenko, A.P.Borisov, V.D.Makhaev, E.I.Mysov, V.B.Shur and M.E.Vol'pin, Izv.Akad.Nauk SSSR, Ser.Khim. (1983) 947

248 M.Kijima, Y.Nambu, T.Endo and M.Okawara, J.Org.Chem. 48 (1983) 2407

249 N.N.Proskina, Z.N.Egorova, N.E.Bulusheva, B.D.Chernishov, G.A.Belenko, Ya.A.Grukov and G.I.Makarova, Tekst.Prom.-st (Moscow) (1982) 56; CA 98 (1983) 5354

250 I.N.Terskaya and V.V.Budanov, Deposited Doc. 1981, SPSTL 924 Khp-D81, 12; CA 98 (1983) 162399

251 K.Nakamura, A.Ohno and S.Oka, Tetrahedron Lett. 24 (1983) 3335

252 G.A.Chukhadzyan, N.A.Balyushina and V.P.Kukolev, Arm.Khim. Zh. 35 (1982) 445; CA 98 (1983) 16244

253 N.Kitamura, Y.Kawanishi and Sh.Tazuke, Chem.Lett. (1983) 1185

254 T.Mashino, T.Nagano and M.Hirobe, Tetrahedron Lett. 24 (1983) 5113

255 S.Ye, F.Han, S.Zhang, S.Qu and S.Wu, Ranliao Huaxue Xuebao 10 (1982) 230; CA 98 (1983) 34045

256 V.N.Belenkov and K.A.Chervinskii, Ukr.Khim.Zh. Russ.Ed. 49 (1983) 868; CA 99 (1983) 175058

257 S.P.Prokopchuk and S.S.Abadzhiev, Visn.L'viv.Politekh.Inst. 171 (1983) 50; CA 99 (1983) 104742

258 S.V.Krylova, L.I.Shcherbak and N.I.Mitskevich, Vestsi Akad. Navuk BSSR, Ser.Khim.Navuk (1983) 22; CA 99 (1983) 69993

259 S.P.Prokopchuk, S.S.Abadzhev and V.U.Shevchuk, Ukr.Khim.Zh. Russ.Ed. 49 (1983) 505; CA 99 (1983) 4987

260 D.H.R.Barton, R.S.Hay-Motherwell and W.B.Motherwell, Tetrahedron Lett. 24 (1983) 1979

261 D.H.R.Barton, J.J.Gastiger and W.B.Motherwell, J.C.S.Chem. Commun. (1983) 41

262 S.Ito and M.Matsumoto, J.Org.Chem. 48 (1983) 1133

263 D.H.R.Barton, M.J.Gastiger and W.B.Motherwell, J.C.S.Chem. Commun. (1983) 731

264 L.G.Jodra, A.Romero, F.Garcia-Ochoa and J.Querol, Ing.Quim. Madrid 14 (1982) 111; CA 98 (1983) 36458

265 Yu.V.Geletii and A.E.Shilov, Kinet.Katal. 24 1983 486; CA 99 (1983) 52841

266 I.M.Krip, B.I.Chernyak and A.I.Klyuchkivskii, Kinet.Katal. 24 (1983) 80

267 A.B.Solov'eva, E.I.Karakozova, K.A.Bogdanova, V.I.Mel'nikova, L.V.Karmilova, G.A.Nikiforov, K.K.Pivnitskii and N.S.Enikolopyan, Dokl.Akad.Nauk SSSR 269 (1983) 160

268 A.Kohda, K.Nagayoshi, K.Maemoto and T.Sato, J.Org.Chem. 48 (1983) 425

269 T.Kobuko, T.Sugimoto, T.Uchida, S.Tanimoto and M.Okano, J.C.S.Chem.Commun. (1983) 769

270 I.A.Krylov, I.Yu.Litvintsev and V.N.Sapunov, Kinet.Katal. 24 (1983) 47

271 Y.Aoyama, T.Watenabe, H.Onda and H.Ogoshi, Tetrahedron Lett. 24 (1983) 1183

272 H.Boennemann, W.Nunez and D.M.M.Rohe, Helv.Chim.Acta 66 (1983) 177

273 M.Bressan, F.Morandini and P.Rigo, J.Organometal.Chem. 247 (1983) C8

274 E.D.Nyberg, D.C.Pribich and R.S.Drago, J.Am.Chem.Soc. 105 (1983) 3538

275 L.Carlton, G.Read and M.Urgelles, J.C.S.Chem.Commun. (1983) 586

276 M.T.Atlay, M.Preece, G.Strukul and B.R.James, Can.J.Chem. 61 (1983) 1332

277 J.Muzart, P.Pale and J.P.Pete, Tetrahedron Lett. 24 (1983) 4567

278 K.Januszkiewicz and H.Alper, Tetrahedron Lett. 24 (1983) 5159

279 K.Januszkiewicz and H.Alper, Tetrahedron Lett. 24 (1983) 5163

280 M.Iriuchijima, Sekiyu Gakkaishi 25 (1982) 349; CA 98 (1983) 53134

281 G.A.Chukhadzhyan, V.P.Kukolev, N.A.Balyushina and L.N.Melkonyan, Arm.Khim.Zh. 35 (1982) 367; CA 98 (1983) 4361

282 W.F.Brill, J.Mol.Catal. 19 (1983) 69

283 E.V.Gusevskaya, V.A.Likholobov, E.P.Talzi and Yu.I.Yermakov, Kinet.Katal. 24 (1983) 53

284 E.V.Gusevskaya, V.A.Likholobov and Yu.I.Yermakov, Kinet. Katal. 24 (1983) 61

285 Yu.A.Aleksandrov, V.M.Fomin and V.Ya.Bordzilovskii, Neftekhimiya 23 (1983) 229; CA 99 (1983) 37844

286 D.Rothe and D.Schnurpfeil, J.Prakt.Chem. 324 (1982) 596; CA 98 (1983) 34172

287 P.Chaumette, H.Mimoun, L.Saussine, J.Fischer and A.Mitschler, J.Organometal.Chem. 250 (1983) 291

288 N.I.Kovtyukhova, V.M.Belousov, S.V.Mikhalovskii, L.D.Kvacheva, Yu.N.Novikov and M.E.Vol'pin, Izv.Akad.Nauk SSSR, Ser.Khim. (1983) 25

289 N.I.Kovtyukhova, V.M.Belousov, Yu.N.Novikov and M.E.Vol'pin, Neftekhimiya 22 (1982) 612; CA 98 (1983) 55972

290 D.Mansuy, M.Fontecave and J.-F.Bartoli, J.C.S.Chem.Commun. (1983) 253

291 A.I.Kamneva, N.V.Koroleva, I.M.Sinitsyna and E.A.Khomyakova, Neftekhimiya 22 (1982) 633; CA 98 (1983) 71242

292 A.I.Kamneva, N.V.Koroleva, I.M.Sinitsyna and L.I.Ryuffer, Neftekhimiya 22 (1982) 798; CA 98 (1983) 197387

293 I.E.Pokrovskaya and T.P.Bashurina, Neftekhimiya 22 (1982) 643

294 S.R.Trusov, M.Austere, M.Roze and O.Neilands, Lat. PSR Zinat.Akad.Vestis, Kim.Ser. (1982) 710; CA 98 (1983) 88915

295 N.G.Ariko, T.P.Kenigsberg and N.I.Mitskevich, Neftekhimiya 22 (1982) 653

296 E.Kwaskowska-Chec and J.J.Ziolkowski, Pol.J.Chem. 55 (1981) 2555; CA 99 (1983) 139121

297 M.Hronec, G.Kiss and J.Sitek, J.C.S.Faraday Trans. I 79 (1983) 1091

298 G.S.Bezhanishvili, N.G.Digurov and N.N.Lebedev, Kinet.Katal. 24 (1983) 1000; CA 99 (1983) 194199

299 T.V.Sirota, L.A.Shvedova and A.B.Gagarina, Izv.Akad.Nauk SSSR, Ser.Khim. (1982) 1987

300 K.Sasaki, S.Ito, Y.Saheki, T.Kinoshita, T.Yamasaki and J.Harada, Chem.Lett. (1983) 37

301 V.P.Morozov and I.V.Smelova, Izv.Vyssh.Uchebn.Zaved.,Khim. Khim.Tekhnol. 26 (1983) 761; CA 99 (1983) 194171

302 T.Kinoshita, J.Harada, S.Ito and K.Sazaki, Angew.Chem. 95 (1983) 504

303 F.F.Shcherbina and N.P.Belous, Kinet.Katal. 24 1983 489; CA 99 (1983) 52842

304 R.P.Wirth, L.L.Miller and W.L.Gladfelter, Organometallics 2 (1983) 1649

305 J.M.Maissant, C.Bouchoule, P.Canesson and M.Blanchard, J.Mol. Catal. 18 (1983) 189

306 T.Funabiki, A.Mizoguchi, T.Sugimoto and S.Yoshida, Chem.Lett. (1983) 917

307 S.Németh, A.Fülep-Poszmik and L.I.Simándi, Acta Chim.Acad. Sci.Hung. 110 (1982) 461

308 S.A.Bedell and A.E.Martell, Inorg.Chem. 22 (1983) 364

309 U.Castellato, S.Tamburini, P.A.Vigato, A.De Stefani, M.Vidali and D.E.Fenton, Inorg.Chim.Acta 69 (1983) 45

310 K.Kushioka, J.Org.Chem. 48 (1983) 4948

311 G.Davies, M.A.El-Sayed and R.E.Fasano, Inorg.Chim.Acta 71 (1983) 95

312 R.D.Willett and G.L.Breneman, Inorg.Chem. 22 (1983) 326

313 P.Capdevielle and M.Maumy, Tetrahedron Lett. 24 (1983) 5611

314 V.P.Nikitin and M.T.Colovkina, Zh.Obshch.Khim. 53 (1983) 1625

315 T.C.Chou and F.S.Lin, Can.J.Chem. 61 (1983) 1295

316 G.P.Chernyuk, V.N.Stan'ko and A.L.Bel'ferman, Neftekhimiya 23 (1983) 243; CA 99 (1983) 7157

317 N.G.Ariko, N.N.Kornilova and N.I.Mitskevich, Vestsi Akad. Navuk BSSR, Ser.Khim.Navuk. (5)(1982) 19 ; CA (1983) 52909

318 J.H.Jensen, J.Am.Chem.Soc. 105 (1983) 2639

319 M.G.Roelofs, E.Wasserman, J.H.Jensen and A.E.Nader, J.Am. Chem.Soc. 105 (1983) 6329

320 G.Speier and Z.Tyeklár, J.C.S.Dalton Trans. (1983) 1995

321 E.M.Kuramshina, V.A.D'yachenko, S.S.Zlotskii and D.L.Rakhmankulov, Neftekhimiya 22 (1982) 620

322 M.Barteri and B.Pispisa, Macromol.Chem.,Rapid Commun. 3 (1982) 715; CA 98 (1983) 17042

323 R.Margalit, I.Pecht and H.B.Gray, J.Am.Chem.Soc. 105 (1983) 301

324 M.D.Aptekar, A.D.Garnovskii and Kh.M.Ismailov, Koord.Khim. 9 (1983) 487

325 G.D.McGinnis, W.W.Wilson, S.E.Prince and C.-C.Chen, Ind.Eng. Chem.Prod.Res.Dev. 22 (1983) 633

326 G.Galliani and B.Rindone, Gazz.Chim.Ital. 113 (1983) 207

327 D.P.Riley, J.C.S.Chem.Commun. (1983) 1530

328 K.A.Askarov, G.G.Tsoi and Ya.L.Simonova, Khim.Prir.Soedin. (1983) 354; CA 99 (1983) 104590

329 A.Nishinaga, S.Yamazaki and T.Matsuura, Chem.Lett. (1983) 1729

330 A.Nishinaga, H.Ohara, H.Tomita and T.Matsuura, Tetrahedron Lett. 24 (1983) 213

331 A.Inada and Y.Morita, Heterocycles 19 (1982) 2139

332 B.Pugin and L.M.Venanzi, J.Am.Chem.Soc. 105 (1983) 6877

333 Y.Nishida, M.Takeuchi, N.Oishi and S.Kida, Inorg.Chim.Acta 75 (1983) 169

334 M.W.Barker and S.I.Perumal, Indian J.Chem.Sect.B 21B (1982) 549; CA 98 (1983) 4170

335 I.Ondrejkovicova, V.Vancova and G.Ondrejovic, Proc.Conf. Coord.Chem. 9th (1983) 321; CA 99 (1983) 70871

336 M.K.Dickson, N.S.Dixit and D.M.Roundhill, Inorg.Chem. 22 (1983) 3130

337 M.E.Vol'pin, M.Yu.Tuvin, Yu.L.Gaft and I.A.Zakharova, Izv. Akad.Nauk SSR, Ser.Khim. (1982) 2177

338 V.Masisi, A.N.Astanina and A.P.Rudenko, Deposited Doc.VINITI 1314-82 (1982); CA 98 (1983) 211739

339 A.N.Astanina, V.Masisi, A.P.Rudenko, G.L.Smirnova, V.D.Kopylova, T.A.Sazykova and E.L.Frumkina, Deposited Doc. 1982, VINITI 2486-82; CA 98 (1983) 179856

340 M.Y.Hamed, J.Silver and M.T.Wilson, Inorg.Chim.Acta 80 (1983) 237

341 V.E.Maizilish, M.K.Islyaikin, V.F.Borodkin, A.M.Mazgarev, V.A.Fomin and A.F.Vil'danov, Zh.Prikl.Khim. (Leningrad) 56 (1983) 2093; CA 99 (1983) 215249

342 G.F.Titova, M.A.Zharnikova and R.P.Smirnov, Izv.Vyssh.Uchebn. Zaved.,Khim.Khim.Tekhnol. 26 (1983) 799; CA 99 (1983) 157621

343 S.M.Paraskewas and A.A.Danopoulos, Synthesis (1983) 638

344 A.Palumbo, G.Nardi, M.D'Ischia, G.Misuraca and G.Prota, Gen. Pharmacol. 14 (1983) 253; CA (1983) 174978

345 N.P.Belous, D.N.Tmenov, T.P.Bepalova, O.V.Alimova and F.F. Shcherbina, Zh.Org.Khim. 19 (1983) 353

346 V.N.Glushakova, N.A.Skorodumova, Yu.O.Gryzina and G.A.Razuvaev, Izv.Akad.Nauk SSSR, Ser.Khim. (1983) 1193

347 A.S.Yakovlev, A.M.Syroezhko, A.A.Vikhorev and V.A.Proskuryakov, Izv.Vyssh.Uchebn.Zaved.,Khim.Khim.Tekhnol. 26 (1983) 121; CA 98 (1983) 142993

348 K.Jitsukawa, K.Kaneda and S.Teranishi, J.Org.Chem. 48 (1983) 389

349 C.S.Reddy and E.V.Sundaram, Gazz.Chim.Ital. 113 (1983) 177; CA 99 (1983) 139120

350 J.T.Groves and T.E.Nemo, J.Am.Chem.Soc. 105 (1983) 6243

351 W.E.Fristad and J.R.Peterson, Tetrahedron Lett. 24 (1983) 4547

352 S.Tamagaki, K.Suzuki, H.Okamoto and W.Tagaki, Tetrahedron Lett. 24 (1983) 4847

353 P.S.Radhakrishnamurti and H.P.Panda, Int.J.Chem.Kinet. 15 (1983) 587; CA 99 (1983) 104563

354 M.Kasai and H.Ziffer, J.Org.Chem. 48 (1983) 2346

355 G.Stork and M.Kahn, Tetrahedron Lett. 24 (1983) 3951

356 P.Müller and C.Bobillier, Tetrahedron Lett. 24 (1983) 5499

357 M.G.Volkhonskii, V.A.Likholobov and Yu.I.Yermakov, Kinet. Katal. 24 (1983) 578; CA 99 (1983) 121619

358 I.P.Stolyarov, M.N.Vargaftik, O.M.Nefedov and I.I.Moiseev, Izv.Akad.Nauk SSSR, Ser.Khim. (1983) 1455

359 D.Dominguez and M.P.Cava, J.Org.Chem. 48 (1983) 2820

360 L.S.Mills and P.C.North, Tetrahedron Lett. 24 (1983) 409

361 V.N.Sapunov, V.G.Sharykin, I.Yu.Litvintsev and N.N.Lebedev, Kinet.Katal. 24 (1983) 853; CA 99 (1983) 194196

362 T.Hiyama and M.Obayashi, Tetrahedron Lett. 24 (1983) 395

363 T.Yokoyama, M.Nishizawa, T.Kimura and T.M.Suzuki, Chem.Lett. (1983) 1703

364 T.L.Siddall, N.Miyaura, J.C.Huffmann and J.K.Kochi, J.C.S. Chem.Commun. (1983) 1185

365 Y.Watanabe, M.Inoue and Y.Itoi, Chem.Pharm.Bull. 31 (1983) 1119; CA 99 (1983) 194153

366 O.Bortolini, F.Di Furia and G.Modena, J.Mol.Catal 19 (1983) 319

367 O.Bortolini, V.Conte, F.Di Furia and G.Modena, J.Mol.Catal. 19 (1983) 331

368 S.Kotov and R.Boeva, Khim.Ind. (Sofia)(1982) 308; CA 98 (1983) 74189

369 V.N.Sapunov, V.G.Sharykin, A.S.Logvinov, I.Yu.Litvintsev and N.N.Lebedev, Kinet.Katal. 24 (1983) 586; CA 99 (1983) 139122

370 S.M.Sobczak, L.Sümegi, I.Nemes and D.Gál, Magy.Kém.Foly. 89 (1983) 112; CA 98 (1983) 215016

371 V.N.Leonov, B.N.Bobylev and G.A.Stozhkova, Neftekhimiya 23 1983 106; CA 98 (1983) 216021

372 G.A.Matveev, V.N.Sapunov, B.R.Serebryakov and N.N.Lebedev, Azerb.Khim.Zh. (1982) (5) 17; CA 99 (1983) 122963

373 S.M.Kulikov and I.V.Kozhevnikov, Kinet.Katal. 24 (1983) 42

374 V.D.Vardanyan, Yu.V.Mitnik, O.A.Miklyaeva, I.Yu.Litvintsev and V.N.Sapunov, Tr.-Mosk.Khim.-Tekhnol.Inst.im.D.I.Mendeleeva 119 (1981) 135; CA 98 (1983) 36466

375 A.Herbowski, J.M.Sobczak and C.C.Ziólkowski, J.Mol.Catal. 19 (1983) 309

376 S.Coleman-Kammula and E.T.Duim-Koolstra, J.Organometal.Chem. 246 (1983) 53

377 M.Spadlo and H.Olkowski, Przem.Chem. 61 (1982) 173; CA 98 (1983) 34448

378 C.Venturello, E.Alneri and M.Ricci, J.Org.Chem. 48 (1983) 3831

379 E.Guilmet and B.Meunier, Nouv.J.Chim. 6 (1982) 511

380 M.-E. De Carvalho and B.Meunier, Tetrahedron Lett. 24 (1983) 3621

381 A.W.van der Made, J.W.H.Smeets, R.J.M.Nolte and W.Drenth, J.C.S.Chem.Commun. (1983) 1204

382 J.T.Groves and T.E.Nemo, J.Am.Chem.Soc. 105 (1983) 5786

383 J.T.Groves and R.S.Myers, J.Am.Chem.Soc. 105 (1983) 5791

384 T.Muto, C.Urano, T.Hayashi, T.Miura and M.Kimura, Chem.Pharm. Bull. 31 (1983) 1166; CA 99 (1983) 139105

385 F.Di Furia, R.Fornasier and U.Tonellato, J.Mol.Catal. 19 (1983) 81

386 C.S.Reddy and E.V.Sundaram, Z.Phys.Chem. (Leipzig) 264 (1983) 737

387 E.S.Huyser and G.W.Hawkins, J.Org.Chem. 48 (1983) 1705

388 S.O.Travin, O.A.Travin, A.P.Purmal, Yu.I.Skurlatov, T.A. Zhemchuzhnikova and Kh.M.Yakubov, Khim.Fiz. (1983) 1247; CA 99 (1983) 164617

389 B.Pispisa, NATO Adv.Sudy Inst.Ser.,Ser.C 100 1983 279; CA 99 (1983) 49503

390 N.N.Pandey, H.Narayan, R.S.Shukla and K.Behari, Z.Phys.Chem. (Leipzig) 263 (1982) 1055; CA 98 (1983) 16140

391 K.Behari, N.N.Pandey, R.S.Shukla and R.K.Dwivedi, Chem.Scr. 20 (1982) 219; CA 98 (1983) 159996

392 S.Kanemoto, K.Oshima, S.Matsubara, K.Takai and H.Nozaki, Tetrahedron Lett. 24 (1983) 2185

393 S.Ito, K.Aihara and M.Matsumoto, Tetrahedron Lett. 24 (1983) 5249

394 P.F.Schuda, M.B.Cichowicz and M.R.Reimann, Tetrahedron Lett. 24 (1983) 3829

395 V.Uma, B.Sethuram and T.N.Rao, Proc.Catsympo 80, Natl.Catal. Symp.,5th 1980, 144; CA 99 (1983) 121589

396 M.P.Doyle, R.L.Dow, V.Bagheri and W.J.Patrie, J.Org.Chem. 48 (1983) 476

397 Y.Tamaru, Y.Yamada, K.Inoue, Y.Yamamoto and Z.Yoshida, J.Org. Chem. 48 (1983) 1286

398 T.Hosokawa, Y.Imada and S.I.Murahashi, J.C.S.Chem.Commun. (1983) 1245; (1984) 264

399 T.Hosokawa, S.Inui and S.Murahashi, Chem.Lett. (1983) 1081

400 S.Jha, P.D.Sharma and Y.K.Gupta, Inorg.Chem. 22 (1983) 1393

401 S.Miyano, L.D.-L.Lu, S.M.Viti and K.B.Sharpless, J.Org.Chem. 48 (1983) 3608

402 Ya.D.Tiginyanu, A.Ya.Sychev and V.I.Oprya, Zh.Neorg.Khim. 27 (1982) 2534

403 C.M.Ashraf, I.Ahmad and F.K.N.Lugemwa, Z.Phys.Chem. (Leipzig) 264 (1983) 794

404 T.Brennan and C.Frenkel, Bot.Gaz. (Chicago) 144 (1983) 32; CA 99 (1983) 194157

405 B.Pispisa, M.Barteri and M.Farinella, Inorg.Chem. 22 (1983) 3166

406 S.Acharya, G.Neogi and R.K.Panda, Int.J.Chem.Kinet. 15 (1983) 867; CA 99 (1983) 194180

407 E.I.Troyanskii, I.V.Svitan'ko, V.A.Ioffe and G.I.Nikishin, Izv.Akad.Nauk SSSR, Ser.Khim. (1982) 2180

408 S.Bhaduri and H.Khwaja, J.C.S.Dalton Trans. (1983) 415

409 A.Arcoria, F.P.Ballistreri, G.A.Tomaselli, F.Di Furia and G.Modena, J.Mol.Catal. 18 (1983) 177

410 T.Takata and W.Ando, Tetrahedron Lett. 24 (1983) 3631

411 M.Anastasia, P.Allevi, A.Fiecchi, G.Galli, P.Gariboldi and A.Scala, J.Org.Chem. 48 (1983) 686

412 T.Takeya, E.Kotani and S.Tobinaga, J.C.S.Chem.Commun. (1983) 98

413 M.Zielinski, Radiochem.Radioanal.Lett. 56 (1983) 45; CA 99 (1983) 121590

414 L.Treindl and M.Mrakavova, Chem.Zvesti 36 (1982) 627; CA 98 (1983) 52928

415 E.S.Rudakov and L.K.Volkova, Kinet.Katal. 24 (1983) 542; CA 99 (1983) 121618

416 J.M.Harris and M.G.Case, J.Org.Chem. 48 (1983) 5390

417 T.Mukaiyama, F.Tabusa and K.Suzuki, Chem.Lett. (1983) 173

418 E.Vedejs, J.M.Dolphin and H.Mastalerz, J.Am.Chem.Soc. 105 (1983) 127

419 E.Vedejs and D.M.Gapinski, J.Am.Chem.Soc. 105 (1983) 5058

420 C.P.Casey, J.C.S.Chem.Commun. (1983) 126

421 J.K.Cha, W.J.Christ and Y.Kishi, Tetrahedron Lett. 24 (1983) 3943

422 W.J.Christ, J.K.Cha and Y.Kishi, Tetrahedron Lett. 24 (1983) 3947

89 J.M.Basset, B.Besson, A.Choplin and A.Theolier, Philos.Trans. R.Soc.London, Ser.A 308 (1982) 115; CA 98 (1983) 96375

90 R.Ganzerla, F.Pinna, M.Lenarda and M.Graziani, J.Organometal. Chem., 244 (1983) 183

91 D.C.Elliott and L.J.Sealock, Ind.Eng.Chem.,Prod.Res.Dev. 22 (1983) 426

92 J.Kaspar, R.Spogliarich, A.Cernogoraz and M.Graziani, J.Organometal.Chem. 255 (1983) 371

93 T.Okano and T.Yoshida, Yuki Gosei Kagaku Kyokaishi 41 (1983) 359; CA 99 (1983) 53950

94 M.A.Radhi, G.Pályi and L.Markó, J.Mol.Catal. 22 (1983) 195

95 E.Alessio, G.Zassinovich and G.Mestroni, J.Mol.Catal. 18 (1983) 113

96 Y.Watanabe, Y.Tsuji, T.Ohsumi and R.Takeuchi, Tetrahedron Lett. 24 (1983) 4121

97 K.Kaneda, T.Imanaka and S.Teranishi, Chem.Lett. (1983) 1465

98 V.P.Baillargeon and J.K.Stille, J.Am.Chem.Soc. 105 (1983) 7175

99 D.J.Darensbourg, C.Ovalles and M.Pala, J.Am.Chem.Soc. 105 (1983) 5937

100 B.Kim and S.L.Regen, Tetrahedron Lett. 24 (1983) 689

101 W.J.S.Lockley, Synth.Appl.Isot.Labeled Compd.,Proc.Int.Symp. (1982) 427; CA 98 (1983) 215266

102 B.J.Fisher and R.Eisenberg, Organometallics 2 (1983) 764

103 A.F.Shestakov and S.M.Vinogradova, Koord.Khim. 9 (1983) 248

104 E.A.Karakhanov, A.G.Dedov, A.S.Loktev, L.V.Popov, P.A.Sharbatyan and I.V.Arkhangel'skii, Khim.Ceterotsikl.Soedin. 1983 754; CA 99 (1983) 87587

105 A.G.Dedov, T.Yu.Filippova, E.B.Neimerovets, L.V.Popov, I.P. Stephanova and E.A.Karakhanov, Khim.Geterosikl.Soedin. (1983) 912; CA 99 (1983) 122210

106 H.Inoue and M.Sato, J.C.S.Chem.Commun. (1983) 983

107 A.R.Brodskii, N.F.Noskova, D.V.Sokol'skii and A.S.Khlystov, Dokl.Akad.Nauk SSSR 286 (1983) 1430

443 P.M.Reddy, V.Jagannadham, B.Sethuram and T.N.Rao, React. Kinet.Catal.Lett. 19 (1982) 243; CA 99 (1983) 139113

444 L.Bencze, J.Kohán and B.Mohai, Acta Chim.Acad.Sci.Hung. 113 (1983) 183; CA 99 (1983) 132706

445 P.R.Rao and E.V.Sundaram, Acta Cienc.Indica, [Ser.] Chem. 8 (1982) 21; CA 98 (1983) 125176

446 I.Ogura, H.Tanaka, M.Yabushita, K.Shimaki, A.Hirai, M.Ozaki and M.Yamaguchi, Kinki Daigaku Genshiryoku Kenkyusho Nempo 19 (1982) 9; CA 98 (1983) 178511

447 J.Yamawaki, S.Sumi, T.Ando and T.Hanafusa, Chem.Lett. (1983) 379

448 D.G.Lee and N.A.Noureldin, J.Am.Chem.Soc. 105 (1983) 3188

449 P.Crotti and F.Machia, J.Org.Chem. 48 (1983) 1350

450 G.A.Fadnis and S.K.Kulshrestha, Carbohydr.Res. 112 (1983) 137; CA 98 (1983) 72617

451 K.Araki, M.Sakuma and S.Shiraishi, Chem.Lett. (1983) 665

452 D.H.Macartney and N.Sutin, Inorg.Chim.Acta 74 (1983) 221

453 L.Omelka, A.Tkac. L.Jirackova and J.Pospisil, Org.Magn.Res., 19 (1982) 153; CA 98 (1983) 53022

454 T.Morimoto and M.Hirano, J.C.S.Perkin Trans.II (1983) 123

455 W.D.Drury and J.M.DeKorte, Inorg.Chem. 22 (1983) 121

456 K.Zaw, M.Lautens and P.M.Henry, Organometallics 2 (1983) 197

457 M.Dagonneau and J.F.Fauvarque, J.Organometal Chem. 241 (1983) 113

458 V.I.Krupenskii, Zh.Obsch.Khim. 53 (1983) 903

459 J.Sykora, M.Jakubcova and Z.Cvengrosova, Coll.Czech.Chem. Commun. 47 (1982) 2061

460 K.Selvaray, K.Ramalingam and K.Ramajaram, J.C.S.Perkin Trans. II (1983) 955

461 M.Puutio and P.O.I.Virtanen, Acta Chem.Scand. A36 (1982) 689; CA 98 (1983) 41389

462 R.Bogoczek and E.Kociolek-Balawejder, Przem.Chem. 61 (1982) 383; CA 98 (1983) 106915

463 G.Rosini and R.Ballini, Synthesis (1983) 543

464 T.Kawasaki, C.S.Chien and M.Sakamoto, Chem.Lett. (1983) 855

465 N.F.Tyupalo and V.V.Zamashchikov, Kinet.Katal. 24 (1983) 909; CA 99 (1983) 175072

466 S.Vivekanandan, K.Venkatarao, M.Santappa and S.Shanmuganathan, Indian J.Chem.,Sect.A 22A (1983) 244; CA 99 (1983) 4985

467 P.K.Kadaba, J.Prakt.Chem. 324 (1982) 857

468 V.Skaric and M.Jokic, Croat.Chem. Acta 56 (1983) 125; CA 99 (1983) 105623

469 E.Burrows and D.H.Rosenblatt, J.Org.Chem. 48 (1983) 992

470 U.Nickel and W.Jaenicke, Ber.Bunsenges., Phys.Chem. 86 (1982) 695; CA 98 (1983) 4158

471 R.J.Stoodley and A.Whiting, J.C.S.Chem.Commun. (1983) 508

472 J.A.Smegal, B.C.Schardt and C.L.Hill, J.Am.Chem.Soc. 105 (1983) 3510

473 J.A.Smegal and C.L.Hill, J.Am.Chem.Soc. 105 (1983) 3515

474 C.Ercolani, M.Gardini, G.Pennesi and G.Rossi, J.C.S.Chem. Commun. (1983) 549

475 C.S.Ameta, H.L.Gupta, P.N.Pande and H.C.Chowdry, Acta.Chim. Acad.Sci.Hung. 110 (1982) 7

476 D.G.Lee and N.S.Srinivasan, Sulfur Lett. 1 (1982) 1; CA 98 (1983) 53128

477 G.A.Ayoko and M.A.Olatunji, Polyhedron 2 (1983) 577

478 G.A.Ayoko and M.A.Olatunji, Inorg.Chim.Acta 80 (1983) L15

479 E.S.Rudakov and V.M.Ignatenko, React.Kinet.Catal.Lett. 22 (1983) 75; CA 99 (1983) 194176

480 M.Suzuki and T.Igarashi, Kanagawa Daigaku Kogakubu Kenkyu Hokoku 21 (1983) 36; CA 99 (1983) 157788

481 L.A.Kozorez, A.G.Zernov and V.A.Yakobi, Izv.Vyssh.Uchebn. Zaved.Khim.Khim.Tekhnol. 25 (1982) 935; CA 98 (1983) 16130

482 R.C.Mohapatra and N.C.Khandual, J.Ind.Chem.Soc. 59 (1982) 1162; CA 98 (1983) 125170

483 D.L.Hickman and H.M.Goff, Inorg.Chem. 22 (1983) 2787

484 S.V.Ley, R.A.Porter, P.F.Gordon and A.J.Nelson, Gen.Synth. Methods 6 (1983) 218

485 A.E.Shilov, Sov.Sci.Rev., Sect. B4 (1982) 71; CA 98 (1983) 124988

486 B.V.Romanovskii, V.Yu.Zakharov and T.G.Borisova, Sovrem. Probl.Fiz.Khim. 13 (1982) 170; CA 98 (1983) 150152

487 E.L.Muetterties and M.J.Krause, Angew.Chem. 95 (1983) 135

488 R.Whyman, Philos.Trans.R.Soc.London, Ser.A 308 (1982) 131; CA 98 (1983) 96312

489 I.V.Kozhevnikov and K.I.Matveev, Appl.Catal. 5 (1983) 135

490 M.L.Khidekel, Sov.Sci.Rev.,Sect. B4 (1982) 283; CA 98 (1983) 136491

491 Yu.N.Nizel'skii and T.E.Lipatova, Probl.Khim.Primen. β-Diketonatov Met. (1978) 213; CA 98 (1983) 60502

492 R.R.Schrock, Science 219 (1983) 13

493 O.N.Temkin and L.G.Bruk, Usp.Khim. 52 (1983) 206; CA 98 (1983) 215633

494 I.I.Moiseev, Sov.Sci.Rev., Sect.B. 1982 4 139; CA 98 (1983) 114390

495 F.R.Hartley and J.A.Davies, Rev.Inorg.Chem. 4 (1982) 27

496 R.J.Cross, Catalysis (London) 5 (1982) 366

497 G.Henrici-Olivé and S.Olivé, J.Mol.Catal. 18 (1983) 367

498 J.R.Blackborow, R.J.Daroda and R.A.Sanchez-Delgado, Acta Cient.Venez. 33 (1982) 131

499 R.Ugo and R.Psaro, J.Mol.Catal. 20 (1983) 53

500 O.A.Tyukova, Khim.Prom-st Rubezhom (1983)(8) 25; CA 99 (1983) 160266

501 N.S.Imyanitov, Khim.Prom-st. (Moscow) (1983) 275

502 G.Consiglio and P.Pino, Top.Curr.Chem. 105 (1982) 77

503 M.G.Katsnel'son, M.L.Kolesov, S.S.Misnik and N.A.Petrov, Khim.Prom-st (Moscow) (1983) 526; CA 99 (1983) 160268

504 C.Lassau, G.Hillion, R.Stern and M.Hellin, Chem.Ind.(Dekker) 5 (1981) 411; CA 98 (1983) 411

505 W.S.Knowles, Acc.Chem.Res. 16 (1983) 106

506 B.D.Vineyard, W.S.Knowles and M.J.Sabacky, J.Mol.Catal. 19 (1983) 159

507 J.Halpern, Pure Appl.Chem. 55 (1983) 99

508 H.Brunner, Angew.Chem. 95 (1983) 921

509 P.Caubere, Angew.Chem. 95 (1983) 597

510 R.C.Wade, J.Mol.Catal. 18 (1983) 273

511 R.C.Wade, Chem.Ind. (Dekker) 5 (1981) 165; CA 98 (1983) 150155

512 E.C.Chukovskaya, R.Kh.Freidlina and N.A.Kuz'mina, Synthesis (1983) 773

513 R.S.Drago, NATO Adv.Study Inst.Ser.,Ser. C 100 (1983) 247; CA 98 (1983) 205024

514 N.S.Enikolopyan, K.A.Bogdanova and K.A.Askarov, Usp.Khim. 52 (1983) 20

515 C.Walling, Oxidases Relat.Redox Syst.,Proc.Int.Symp.3rd 1979, (1982) 85; CA 98 (1983) 121709

516 G.A.Kuvtun and I.I.Moiseev, Khim.Prom-st. (Moscow) 2 (1983) 71

517 A.Vlcek, Proc.Conf.Coord.Chem. 9th (1983) 449; CA 99 (1983) 77506

518 R.A.Sheldon, J.Mol.Catal. 20 (1983) 1

519 A.De, J.Sci.Ind.Res. 41 (1982) 484; CA 98 (1983) 33894

520 E.S.Gore, Platinum Met.Rev. 27 (1983) 111

521 L.V.Levchenko and Z.M.Zavorokhina, Tr.Inst.Khim.Nauk, Akad. Nauk Kaz.SSR 57 (1982) 168

522 J.E.Bäckvall, Acc.Chem.Res. 16 (1983) 335

523 A.D.Zuberbuehler, Copper Coord.Chem.: Biochem.Inorg.Perspect. (1983) 237; CA 99 (1983) 77513

524 G.Davies and M.A.El-Sayed, Copper Coord.Chem.: Biochem. Inorg.Perspect. (1983) 281; CA 99 (1983) 77514

525 J.A.R. Van Veen and J.F.Van Baar, Rev.Inorg.Chem. 4 (1983) 293

Corrigendum

References 495-521 are missing from the 1982 Annual Survey. These are compiled below.

495 E.L.Muetterties, Chem.Soc.Rev. 11 (1982) 283

496 E.Cesarotti, R.Ugo and L.Kaplan, Coord.Chem.Rev. 43 (1982) 275

497 T.H.Black, Aldrichimica Acta 15 (1982) 13; CA 97 (1982) 5399

498 S.D.Jackson, P.B.Wells, R.Whyman and P.Worthington, Catalysis (London) 4 (1981) 75

499 T.J.Thomas, D.A.Hucul and A.Brenner, ACS Symp.Ser. 192 (1982) 267; CA 97 (1982) 61675

500 F.Ciardelli, G.Braca, C.Carlini, G.Sbrana and G.Valentini, J.Mol.Catal. 14 (1982) 1

501 L.B.Ebert, J.Mol.Catal. 15 (1982) 275

502 E.G.Chepaikin and M.L.Khidekel, Koord.Khim. 8 (1982) 1011; CA 97 (1982) 134172

503 K.H.Keim, J.Korff, W.Keim and M.Roeper, Erdöl Kohle, Erdgas, Petrochem. 35 (1982) 297; CA 97 (1982) 129388

504 H.Bahrmann and W.Lipps, Chem.-Ztg. 106 (1982) 249; CA 97 (1982) 57457

505 M.F.Mirbach, M.J.Mirbach and A.Saus, Chem.Rev. 82 (1982) 59

506 J.Halpern, Acc.Chem.Res. 15 (1982) 332

507 R.H.Crabtree, CHEMTECH 12 (1982) 506

508 E.I.Klabunovskii, Usp.Khim. 51 (1982) 1103; CA 97 (1982) 161820

509 N.Izumiya, ACS Symp.Ser. 185 (1982) 272; CA 97 (1982) 72720

510 T.Hayashi and M.Kumada, Acc.Chem.Res. 15 (1982) 395

511 M.Kumada, T.Hayashi and K.Tamao, Fundam.Res. Organomet.Chem. Proc. China-Jpn-US. Trilateral Semin. Organomet.Chem. 1st 1980, 175; CA 97 (1982) 127671

512 M.Kumada, T.Hayashi and K.Tamao, Stud.Org.Chem.(Amsterdam) 6 (1981) 55; CA 96 (1982) 180215

513 B.Bosnich and M.D.Fryzuk, Top.Stereochem 12 (1981) 119; CA 96 (1982) 180224

514 K.Drauz, A.Kleeman and J.Martens, Angew.Chem. 94 (1982) 590

515 D.V.Korol'kov, Izv.Sib.Otd.Akad.Nauk. SSSR, Ser.Khim.Nauk (1982) 4, 54; CA 97 (1982) 116007

516 H.Mimoun, Chem.Phys. Aspects Catal.Oxid. [Proc.Spring Sch. CNRS Catal.Oxid.] 1978 (Pub 1980) 15; CA 97 (1982) 45010

517 D.Hoppe, Nachr.Chem.Tech.Lab. 30 (1982) 281; CA 96 (1982) 217605

518 J.J.Ziolkowski, Oxid.Commun. 2 (1982) 307; CA 97 (1982) 181312

519 D.G.Lee, Org.Chem. (N.Y.) 5 (1982) 147; CA 97 (1982) 181262

520 H.Gampp and A.D.Zuberbuehler, Met.Ions Biol.Syst. 12 (1981) 133; CA 96 (1982) 11994

521 H.Mimoun, Angew Chem. 94 (1982) 750