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Review

Transition metal catalyzed hydrogenation or reduction in water

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Abstract

This paper summarizes recent reports on (i) hydrogenation (including transfer hydrogenation by HCO_2Na) of olefins or aldehydes in water, and (ii) reduction of aromatic nitro compounds with carbon monoxide and water by homogeneous transition metal catalysts. The discussion will be focused on the hydrogenation of α,β-unsaturated aldehydes by ruthenium–sulfonated phosphine complexes that show remarkable chemoselectivity toward C=O bonds. The author also introduces selective reduction of aromatic nitro-groups by ruthenium or rhodium catalysts under CO/H_2O conditions. These catalytic reactions are very important from both synthetic and industrial viewpoints, not only because the after-treatment of by-products can be simplified from the conventional methods, but also because the reaction also proceeds with high selectivity affording the desired products. © 1998 Elsevier Science B.V.

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1. Introduction

The use of water in organic synthesis attracts particular attention, not only because transformations are included for which hydrophobic effects might be invoked as the activation factor, but also because transformations where water leads to valuable changes compared to the traditional solvents are included [1]. Since 60–70% of all the industrial chemicals are produced using a catalytic process at some stage in their manufacture and 10–15% of these involve homogeneous catalysis [2], considerable interests have thus been focused, especially recently, on organometallic catalysis in aqueous media, as already introduced by Cornils and Wiebus [3], and Haggin [4]. The potential importance of these catalyses should be recognized, as we can also easily understand from several papers [1,5–9] summarizing recent reports in this research field, and from the special issue [10] in this journal.

The use of water in homogeneous catalytic reactions has also an important role, in order for industrial process to emphasize an attractive nature of the catalysis, as already developed by Rhone-Poulenc for hydroformylation using rhodium catalysts (ex. propene to *n*-butanal by rhodium–TPPTS: TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$) (For examples of this background [11–22]), or by the Kuraray Company for hydrodimerization (examples for background of this process: [23–25]) using palladium catalysts (ex. butadiene to 2,7-octadienol by palladium/phosphonium salts). Water-soluble ligands plays an important key role for these catalyses especially for separation; the products can thus easily be obtained by simple phase separation.

Recently, remarkably high chemoselectivity is observed for the hydrogenation of olefins, aldehydes by homogeneous rhodium or ruthenium catalysts carried out in water. The selective reduction of aromatic nitro compounds by rhodium or ruthenium catalysts under CO/H_2O conditions has also been reported. These catalytic reactions should be appreciated due to not only their high selectivities but also their simplified chemical processes compared to the conventional methods, as mentioned below. From these backgrounds, the author has therefore summarized recent papers for transition metal catalyzed hydrogenation and reduction of unsaturated bonds (C=C, C=O, and aromatic nitro groups) in aqueous media.

2. Catalytic hydrogenation of olefins and reduction of aldehyde with CO– or H_2–H_2O ($HCOONa/H_2O$)

2.1. Hydrogenation of olefins

Catalytic organic synthesis in two-phase systems is very important especially from practical viewpoints for separating the desired products from the catalyst. Since the early works, particularly by Wilkinson et al. on $[RhCl(PPh_3)_3]$, it is known that varying the coordination sphere of the metal center can induce high selectivities [26]. One of their applications of two-phase systems involved the hydrogenation of olefins catalyzed by transition metal complexes containing the mono- or tri-sulfonated *tert*-phosphine. These studies were extended to asymmetric hydrogenations using water-soluble chiral ligands, and revealed a peculiar role played by water on the enantiomeric excess. Examples of the recent reports for catalytic hydrogenation or transfer hydrogenation of olefins were summarized in Table 1.

Borowski et al. have reported the hydrogenation of 1-hexene, *cis*/*trans*-2-hexene and cyclohexene catalyzed by rhodium or ruthenium complexes in a two-phase (olefin and water) medium without cosolvent [27]. Two catalysts, $[RhCl(TPPMS)_3]$ and $[RuHCl(TPPMS)_3]$ (TPPMS = $Ph_2P(m$-

Table 1
Examples of recent reports for hydrogenation of olefins by homogeneous catalyst systems under H_2 /H2O or HCO_2Na/H_2O conditions

Catalysts	Substrates etc.	Ref.
Hydrogenation of C=C (H_2 /H_2O)		
$RhCl(TPPMS)_3$, $RuHCl(TPPMS)_3$, TPPMS = $Ph_2P(m\text{-}C_6H_4SO_3Na)$	1-hexene, cyclohexene, *cis*- and *trans*-2-hexene	[27]
$RhCl_3 \cdot 3H_2O$/TPPMS	cyclohexene	[28]
metal/phosphine	octene (kinetic study, water–octene system)	[29]
$RhCl_3$ /TPPTS, TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$	cyclic, linear olefins, polyenes	[30,31]
cis, fac-$[RhH_2(H_2O)(TPPPS)_3]^+$	olefins	[32]
Rh/TPPMS/maleic or fumaric acid	olefins	[34]
$[Rh(NBD)(amophos)]^{3+}$, amophos = $Ph_2PCH_2CH_2NMe_3$	1-hexene	[35,36]
$RuCl_2(TPPMS)_2$, $RuHCl(TPPMS)_3$ etc.	styrene, cyclohexene	[37]
$[HRu(CO)Cl(TPPMS)_3] \cdot 2H_2O$ etc.	styrene, cyclohexene	[38]
$[RuCl(\mu\text{-}Cl)(TPPTS)_2]_2$ etc.	olefins, α,β-unsaturated ketones	[39]
Palladium acetate/triethoxylsilane	alkene, alkyne	[40,41]
Pd-di(sodium alizarinmonosulfonate)	unsaturated fatty acids esterified in lipids	[42]
$Rh(NO)(TPPTS)_3 \cdot 9H_2O$ etc.	cyclohexene etc.	[43,44]
$(Cy_3P)_2RhHCl_2$	selective hydrogenation of C=C for α,β-unsaturated aldehydes	[45]
$RhCl[P(p\text{-}CH_3C_6H_4)_3]_3$	3,8-nonadienoic acid to 8-nonenoic acid (water as additive)	[46]
$[RhCl(Ph_2P(CH_2)_nCOONa)_2]_2$, $n = 6$ or 8	olefins, polybutadiene	[47]
cis, mer-$(Me_3P)_3IrH_2Cl$	alkenes, alkynes	[121,122]
$RhCl_3$ /octylamine/$(Me_2CHCH_2)_2AlH$	1-hexene, cyclopentene, cyclohexene, isoprene, 2-heptene	[123]
Rh/β-P(O)substituted 1-phosphanorbornadienes etc.	(*Z*)-α-(*N*-acetamido)cinnamic acid	[124]
Rh/TPPMS	fumaric, maleic, and crotonic acids	[125]
[Ru(binap-$4SO_3Na$)(benzene)Cl]Cl, binap = (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphtyl	2-acylamino acid precursors, methylene succinic acid	[126]
$[Rh(COD)_2]BF_4$ /1.1eq. BPPM, BPPM = (2S,4S)-4-diphenylphosphino-2-diphenylphosphinomethylpyrrolidine	(*Z*)-Me-a-acetamidocinnamate to (*R*)-(+)-*N*-acetylphenylalanine Me ester 96% ee	[127]
Rh/sulfonated-binap	2-acetamidoacrylic acid, methyl ester	[128]
Rh/cationic phosphine, cationic phosphine = (*S,S*)-2,4-bis[bis(*p-N,N,N*-trimethylammoniumphenyl)phosphino]pentane	(*Z*)-RCH=C(CO_2H)NHAc, R = 3,4-MeO(AcO)C_6H_3, 95% ee	[129]
$[Rh(COD)L]^{2+} \cdot 2BF_4^-$, L = (3*R*,4*R*)-bis(diphenylphosphino)pyrrolidine by *N*-methylation	(*Z*)-PhCH=C(NHAc)CO_2R (R = H, Me) 87–96% ee	[130]
$[MX_nQ(SO_3A\text{-binap})]Y$, M = Ru, Ir, Rh, Pd etc; A = alkali metal atom; X = halogen, $n = 0,1$; Q = benzene, *p*-cymene, Y = halogen, ClO_4, PF_6, BF_4	enantioselective hydrogenation (patent claimed)	[131]
$[RhCl(COD)]_2$ /L, L = sulfonated 1,2-bis(diphenylphosphinomethylene)-cyclobutane	*Z*-α-acetamidocinnamic acid to *N*-acetylphenylalanine 51% ee	[132]
Polymer-supported catalysts (H_2 /H_2O or HCO_2Na/H_2O)		
Ru–Cr/polyaluminazane etc.	ethylbenzoate to cyclohexylcarbitol (H_2 /water as additives)	[133]
$[Ph_2P(CH_2CH_2O)_{n-1}CH_2CH_2PPh_2]_{1.5}RhCl$	allyl alcohol, H_2 /H_2O	[134]
Ru(binap-$4SO_3Na$)-SAP (polymer supported)	2-(6′-methoxy-2′-naphthyl)acrylic acid to naproxen, 96% ee (H_2 /H_2O)	[76,77]
R_3RhCl, R_2RuCl_2, R_4Pt etc. (R = Ph_3P)/chloromethylated styrene–divinylbenzene/Li3P	reduction by HCO_2H, HCO_2Na/H_2O 1-heptene, CH_2=CHR′ (R′ = CHO, CH_2OH, OAc, OBu)	[135]

Table 2
Hydrogenation of alkenes with TPPMS containing complex catalysts [27]

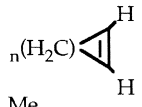
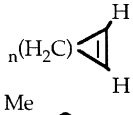
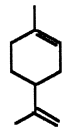
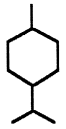
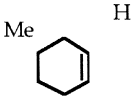
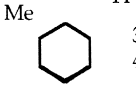
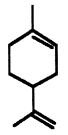
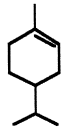
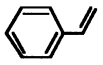
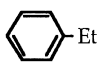
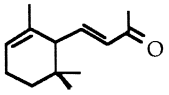
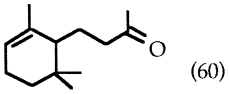
Catalyst [a]	Conc. [b]	Temp. [c] °C	Starting alkene	Product distribution (%)		
				hexane	*trans*-2-hexene	*cis*-2-hexene + 1-hexene
1	1.9	25	1-hexene	72.5	22.5	5
1	2.4	25	*cis*-/*trans*-2-hexene [d]	9	29	62
1	2.3	25	cyclohexene	14 [e]	86 [f]	
2	2.9	80	1-hexene	55	13	32
2	3.4	80	*cis*-/*trans*-2-hexene [d]	31	28	41
2	3.6	80	cyclohexene	21 [e]	79 [f]	

Reaction conditions: Catalyst dissolved in water (10 ml), olefin 3 ml, H_2 3 atm, 24 h.
[a] Catalyst **1**: $RhCl(TPPMS)_3 \cdot 4H_2O$, Catalyst **2**: $RuHCl(TPPMS)_3 \cdot 2H_2O$. TPPMS = $Ph_2P(m\text{-}C_6H_4SO_3Na)$.
[b] Conc.: mmol/l.
[c] ±5°C.
[d] Mixture of *cis*/*trans* = 87/13%.
[e] Cyclohexane.
[f] Cyclohexene.

$C_6H_4SO_3Na$), were employed and the former was shown to be the more effective and selective catalyst for terminal alkenes (Table 2). However, significant amounts of internal alkenes isomerized were obtained from hexenes, probably due to the absence of cosolvent. Air must be carefully excluded, because the Rh(I) and Ru(II) complexes are sensitive to the air. Dror and Manassen also showed the hydrogenation of cyclohexene in a two-phase system catalyzed by $[RhCl_3 \cdot 3H_2O]$ + TPPMS in the presence of cosolvent [28]. The activity of the catalyst depended on the cosolvent and increased in the order: dimethylacetamide < dimethoxymethane < ethanol < methanol, the conversion being as high as 90% in the last one. Calculations for ternary diagrams of water/1-octene/cosolvent systems were made by Halbot et al. [29]. They described that methanol and ethanol are especially effective to solubilize 1-octene in the aqueous phase, whereas the solubility of water in the organic phase is maintained at a very low level. It is concluded that the catalytic reaction does not occur in the interface but in the aqueous phase, because higher catalytic activities are exhibited in the presence of better cosolvents. Joo and coworkers, doing research on, the kinetics of the hydrogenation of crotonic, maleic and fumaric acid by $[RhCl(TPPMS)_3]$, then suggested the reaction scheme in these catalytic reactions [30]. However, they reported an interesting observation, later in the hydrogenation of maleic acid or fumaric acid by $RhCl(TPPMS)_3$, that TPPMS and these olefins gave the corresponding phosphonium salt, which presumably promoted the formation of the catalytically active species [31].

Larpent et al. also showed that various olefins were hydrogenated with 100% conversion by another analog of Wilkinson's complex ($RhCl_3$ + TPPTS; TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$). The catalytic reaction exhibited complete selectivity of the C=C bond regardless the identity of the various functional groups (Table 3) [32]. ^{31}P NMR analyses showed that oxidation of TPPTS occurred very quickly so that colloidal dispersions of rhodium stabilized by oxide, $O{=}P(m\text{-}C_6H_4SO_3Na)$, worked as the catalytically active species. Further studies showed that dihydride species $[RhH_2Cl(TPPTS)_3]$ (*cis*-mer and *cis*-fac isomers) had disappointing catalytic activity [33]. No hydrogenation took place unless sufficient amounts of phosphine oxide had been produced. Therefore, when Rh(III) complexes were used as catalytic precursors, actual catalytic species were attributed to metallic rhodium particles dispersed and stabilized by sulfonate anions, which prevented the metal species from aggregating, as shown by the hydrogenation of cycloheptene studied by ^{31}P NMR and light-scattering measurements [34].

Table 3
Catalytic hydrogenation of olefins [30]

Olefin	Product (a)	Olefin	Product (a)
	 n = 3 (8), 5 (8), 6 (7)		 (76)
	 3-Me (5) 4-M4 (10)		 (32)
	 (40)		 (60)
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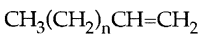
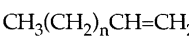
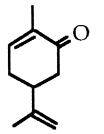
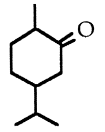
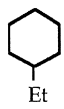
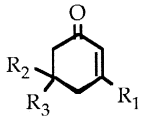
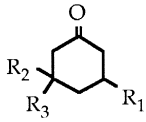
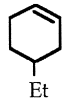
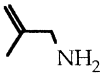
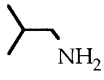
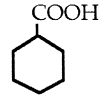
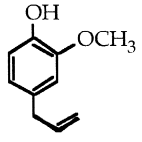
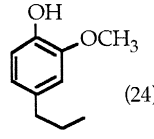
	 n = 5 (13), 12 (60)		 (42)
	 (48)		 R_1=R_2=R_3 =H (13) R_1=Me, R_2=R_3=H (14) R_1=R_2=Me, R_3 =H (17) R_1=R_2=R_3=Me (18)
	 (20)		
	 (15)		 (18)
	 (24)	 oleic acid	 (16) stearic acid (12)

Reaction conditions: 50 mg of catalyst (prepared from $RhCl_3 \cdot 3H_2O$ + TPPTS), water 3 ml, olefin 10 mmol. (a): in blankets, reaction time in hour for 100% conversion, the isolated yield of purified products are in the range 90–95%.

In contrast with the rhodium catalysts containing TPPMS (TPPMS = $Ph_2P(m\text{-}C_6H_4SO_3Na)$, the amphos systems (amphos = $Ph_2PCH_2CH_2N^+Me_3$) are much more stable to oxidation by air, and can even be handled in air and recycled without special precautions [35,36]. They reported that $[Rh(NBD)(amphos)_2]^{3+}$ (NBD = norbonadiene) was obtained from the reaction of $[Rh(NBD)Cl]_2$ with four equivalents of amphos nitrate. The species, $[Rh(NBD)(amphos)_2]^{3+}$, behaved like its triphenylphosphine analog, and isomerized 1-hexene into internal olefins (10–20%). In this case, the activity of the catalyst was strongly dependent on the organic solvent; the reaction in Et_2O was more efficient than that in *n*-heptane, possibly due to its better solubility in water. *n*-Heptane displayed higher efficiency as a solvent than dichloromethane, which could even present an inhibiting effect.

The aqueous phase involving the catalytically active species could be reused, because only 0.1% of the catalyst leaked into the organic layer. Maleic and crotonic acids were also hydrogenated at 1 bar, and the reactions proceeded at a rate faster than that by the analogous rhodium complexes containing TPPMS. Furthermore, the catalytic activities are higher in methanol than in water, probably either due to the higher solubility of dihydrogen in methanol or lower solubility of $[RhH_2(amphos)_2(H_2O)_2]^{3+}$ in water as compared with $RhH_2(amphos)_2(MeOH)_2]^{3+}$. An excess amount of amphos should not be added because it prevents olefin coordination.

Joo and coworkers reported that ruthenium complexes such as $RuCl_2(TPPMS)_2$, $RuHCl(TPPMS)_3$ and $RuH(OAc)(TPPMS)_3$ catalyzed the hydrogenation of 1-hexene and styrene under similar conditions with much slower rates than $RhCl(TPPMS)_3$ [37]. Andriollo characterized $RuHCl(TPPMS)_3$, and employed it as the catalyst for hydrogenations of styrene (turnover/h 3.0; 86% conversion), cyclohexene (turnover/h 1.1; 25% conversion) in a water/decaline mixture [38].

Recently, Kalck et al. showed the selective hydrogenation of the C=C double bond of α,β-unsaturated ketone (4-hexen-3-one and benzylideneacetone) by $[RuCl(\mu\text{-}Cl)(TPPTS)_2]_2$ in H_2O [39]. The selectivity of the olefinic bond was increased upon the addition of $SnCl_2$ (substrate: 4-hexen-3-one), although the selectivities decreased in the presence of LiOH, or KOH.

Water soluble alkenes and alkynes such as unsaturated acids were also reduced in good yields by palladium acetate and triethoxysilane at room temperature in water [40] and substrates poorly soluble in water could be hydrogenated in water–THF solvent systems [41]. Alkynes could be reduced to alkenes by triethoxysilane as the hydrogen source. The reaction, however, required a careful control of the amount of triethoxysilane in the reaction. Joo et al. reported palladium di(sodium alizarinmonosulfate) is a highly efficient catalyst for the hydrogenation of the C=C bond of unsaturated fatty acids esterified in lipids of modal or biological membranes, enabling the study of the relationship between function and the physical state of membranes [42].

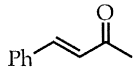
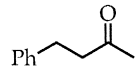
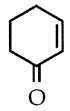
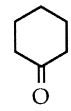
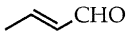
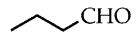
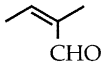
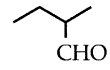
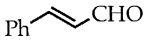
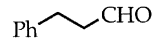
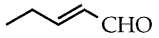
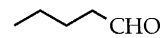
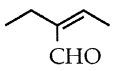
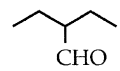
Syntheses of various transition metal complexes containing trisulfonated-triphenylphosphine (TPPTS) were reported by Herrmann et al. [43,44] (examples: $Pd(TPPTS)_3 \cdot 3H_2O$, $Rh_6(CO)_7(TPPTS)_9 \cdot 27H_2O$, $Rh(NO)(TPPTS)_3 \cdot 9H_2O$, $PtCl_2$-$(TPPTS)_2 \cdot 6H_2O$, $Ru(NO)_2(TPPTS) \cdot 6H_2O$, $Pt(TPPTS)_4 \cdot 12H_2O$, $RhCl(CO)(TPPTS)_2 \cdot 6H_2O$, $RhCl(TPPTS)_3 \cdot 9H_2O$, $Rh(CH_3COO)(TPPTS)_3 \cdot 9H_2O$, $(\eta^4\text{-}C_8H_{12})(\mu\text{-}Cl)_2Rh_2$-$(TPPTS)_2 \cdot 6H_2O$, $Au_2(TPPTS)_2S \cdot 6H_2O$, $(\eta^4\text{-}C_8H_{12})IrCl(TPPTS)_2 \cdot 6H_2O$, $Co_2(CO)_6$-$(TPPTS)_2 \cdot 6H_2O$, $CoH(CO)(TPPTS)_2 \cdot 9H_2O$, $CoH_2(TPPTS)_3 \cdot 9H_2O$, $Ni(CO)_2(TPPTS)_2 \cdot 6H_2O$, $Ni(TPPTS)_3 \cdot 9H_2O$). The hydrogenation of cyclohexene and 1-octene by $Rh(NO)(TPPTS)_3 \cdot 9H_2O$ or cobalt complexes, and reduction of nitrobenzene with CO and water by $Fe_2(CO)_9$-TPPTS were examined [43,44]. However these complexes showed low catalytic activities.

Alper et al. reported that the rhodium complex $(Cy_3P)_2Rh(H)Cl_2$ was an effective catalyst precursor for selective hydrogenation of the C=C double bonds of α,β-unsaturated aldehydes or ketones under mild conditions as shown in Table 4 [45]. It was also revealed that water or 0.5 N NaOH aqueous solution is indispensable for generating catalytically-active species. Addition of an inorganic base would drive the equilibrium between the mono- and dihydride species (Eq. (1)) to the latter side.

$$L_2Rh(H)Cl_2 + H_2 \underset{\substack{L=\\ Cy_3P}}{\rightleftharpoons} L_2Rh(H)_2Cl + HCl \quad (1)$$

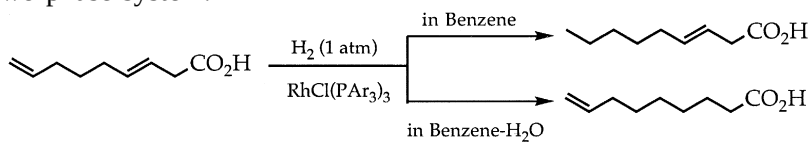
Okano et al. reported an interesting example for the regioselective hydrogenation of 3,8-nonadienoic acid with $RhCl[P(p\text{-tolyl})_3]_3$ (Eq. (2), Table 5) [46]. Addition of water to the complex/benzene/H_2 (1 atm) system caused a significant change in the product distribution. The terminal olefin

Table 4
Hydrogenation of α,β-unsaturated carbonyl compounds by $(Cy_3P)_2Rh(H)Cl_2$ (**1**) and H_2O or NaOH at 1 atm [45]

substrates (amount/mmol)		amt of **1** mol %	promoter (amt/ ml)	solvent (amt/ ml)	temp. /°C	time /h	product	GC yield (conv./%)
	(1)	1	0.5N NaOH (0.5)	benzene (2)	50-55	20		93[a] (100)
	(2)	0.5	0.5N NaOH (0.2)	benzene (2)	25	11		96 (100)
	(2)	1	0.5N NaOH (0.2)	benzene (2)	25	18		90 (100)
	(2)	1	H_2O (0.2)	m-xylene (2)	25	22		81 (100)
	(2)[b]	1	H_2O (1)	m-xylene (2)	25	48		95 (100)
	(2)	2	H_2O (0.5)	benzene (2)	35	22		60 (66)
	(2)	1	H_2O (0.2)	m-xylene (2)	25	21		35 (35)
		5	H_2O (0.2)	m-xylene (2)	25	48		90 (100)
	(2)	5	H_2O (0.2)	neat	25	40		15 (15)

[a] Isolated yield.
[b] Rhodium metal deposited approximately 24 h after the reaction began.

was reduced to afford 3-nonenoic acid, whereas 8-nonenoic acid became the major product in the water/benzene two phase system.



(2)

Rempel et al. recently reported that $[RhCl(Ph_2P(CH_2)_nCO_2Na)_2]_2$ [$n = 6$ (HEXNa), or $n = 8$ (OCTNa)] showed remarkable catalytic activities for the hydrogenation of olefins and low molecular weight polymers in water [47]. The $[RhCl(HEXNa)_2]_2$ complex showed higher catalytic activities; the order of the reaction rate for various substrates is as follows: terminal olefins > internal olefins > cyclic olefins (Table 6). 1,2-Addition units in polybutadiene ($M_n = 900$) were selectively hydrogenated over

Table 5
Regioselective hydrogenation of 3,8-nonadienoic acid under two-phase conditions [46]

Catalyst	Water (ml)	Time (h)	Conv. (%)	Yield (%) [a] of		
				3-nonenoic	8-nonenoic	nonanoic acids
$RhCl(PPh_3)_3$	0	4.0	89	57	12	24
$RhCl(PPh_3)_3$	0.003 [b]	3.8	83	52	17	24
$RhCl(PPh_3)_3$	5.0	2.5	90	6	75	16
$RhCl[P(p\text{-tolyl})_3]_3$	0	4.0	78	66	10	20
$RhCl[P(p\text{-tolyl})_3]_3$	0.5	4.0	77	13	54	27
$RhCl[P(p\text{-tolyl})_3]_3$	2.0	3.8	80	4	76	13
$RhCl[P(p\text{-tolyl})_3]_3$	5.0	3.2	86	1	84	8
$RhCl[P(p\text{-tolyl})_3]_3$	10.0	0.25	17	6	86	2
$RhCl[P(p\text{-tolyl})_3]_3$	10.0	2.0	90	0.7	85	8
$RhCl[P(p\text{-tolyl})_3]_3$	10.0	6.0	98	0.5	81	15

Reaction conditions: $RhCl(PAr_3)_3$ 0.025 mmol, 3,8-nonadienoic acid 2.5 mmol, benzene 5.0 ml, H_2 1 atm, 30°C.
[a] The yields were based on conversion.
[b] A benzene solution saturated with water at 25°C was used.

the 1,4-(internal)addition units by these catalysts. An extensive study to the hydrogenation of other polymers would be expected.

2.2. Reduction of aldehydes

Recent reports for the reduction of aldehyde in water are summarized in Table 7. The pioneering work was reported by Joo and coworkers for the reduction of pyruvic acid using a ruthenium–TPPMS catalyst [48]. They reported later that $[HRuCl(TPPMS)_3]$ was an effective catalyst for chemoselective hydrogenations of 2-keto acids (hydrogenation of the ketonic function of pyruvic, phenylpyruvic, 2-ketopentanoic, 2-ketooctanoic acids) [49]. Turnover numbers of 1300 were reported for the catalytic hydrogenation of pyruvic acid affording lactic acid (Eq. (3)).

$$CH_3COCO_2H + H_2 \xrightarrow[1\,bar,60^\circ C,pH\,1]{HRuCl(TPPMS)_3} CH_3CH(OH)CO_2H \quad (3)$$

Darensbourg et al. reported that the water-soluble *cis*-$RuCl_2(PTA)_4$ (PTA = 1,3,5-triaza-7-phosphaadamantane) was also an effective catalyst for hydrogenation of unsaturated aldehyde affording unsaturated alcohol in the presence of HCO_2Na/H_2O [50]. This catalyst, *cis*-$RuCl_2(PTA)_4$, could be easily prepared from hydrated ruthenium trichlorides or $RuCl_2(PPh)_3$ with the ligand (PTA),

Table 6
Catalytic hydrogenation of olefins in water with $[RhCl(Ph_2P(CH_2)_6COONa)_2]_2$ complex [47]

Substrate	Product	Yield(%)	TOF [a]
1-Octene [b]	n-octane	94	1880
1-Decene [b]	n-decane	92 (2 h)	920
Styrene [b]	ethylbenzene	100	2000
α-Methylstyrene	isopropylbenzene	15	300
trans-3-Pentenenitrile	valeronitrile	99	1880
cis-2-Pentenenitrile	valeronitrile	99 (15 min)	7920
cis-2-Heptene	heptane	41	820
trans-2-Heptene	heptane	33	660
Cyclooctene	cyclooctane	13	260

Reaction conditions: complex 0.01 mmol, olefin 40 mmol, water 80 ml, 90°C, H_2 4 MPa, reaction time 1 h otherwise indicated.
[a] TOF: number of moles of olefins hydrogenated per mole of Rh in 1 h.
[b] at 50°C.

Table 7
Examples of recent reports for reduction of aldehydes by homogeneous catalysts in aqueous media

Catalysts	Substrates etc.	Ref.
Hydrogenation of C=O group (H_2/H_2O)		
Ru/TPPMS, TPPMS = $Ph_2P(m\text{-}C_6H_4SO_3Na)$	pyruvic acid	[48]
$HRu(OAc)(TPPMS)_3$, $RuCl_2(TPPMS)_2$, $HRuCl(TPPMS)_3$	2-keto acids	[49]
$[RuCl_2L_2]_2$, $RuHClL_3$, $RuH(OAc)L_3$, RuH_2L_4, $RuHIL_3$, $RuCl_2(CO)_2L_2$, $[Ru(OAc)(CO)_2L]_2$, L = $P(m\text{-}C_6H_4SO_3Na)_3$ (TPPTS)	propionaldehyde	[51–53]
cis-$[Ru(6,6'\text{-}Cl_2bpy)_2(OH_2)_2](CF_3SO_3)_2$, 6,6′-$Cl_2$bpy = 6,6′-dichloro-2,2′-bipyridine	acetophenone etc. aldehyde, olefins	[136,137]
$RuCl_3$/TPPTS	hydrogenation of α,β-unsaturated aldehydes	[70]
$H_2RuCl_2(PPh_3)_4$ etc.	hydrogenation of all-*trans*-retinal to all-*trans*-retinol	[71]
$RuCl_2(TPPTS)_3/SiO_2$, $RuH_2(TPPTS)_4/SiO_2$ etc.	hydrogenation of α,β-unsaturated aldehydes to alcohols	[72]
$RuCl_3$/TPPTS, $[RhCl(COD)]_2$/TPPTS	hydrogenation of α,β-unsaturated aldehydes	[73]
$[RuCl(\mu\text{-}Cl)(TPPTS)_2]_2$ etc.	hydrogenation of α,β-unsaturated compounds	[39]
$OsH_4(TPPMS)_3$, $OsHCl(CO)(TPPMS)_2$, $[OsCl_2(TPPMS)_2]_2$ etc.	hydrogenation of α,β-unsaturated compounds	[74]
Transfer hydrogenation of C=O group by HCO_2Na/H_2O		
cis-$RuCl_2(PTA)_4$, PTA = 1,3,5-triaza-7-phosphaadamantane	benzaldehyde, methylbenzaldehyde etc. HCO_2Na/H_2O	[50]
$RuCl_2[Ph_2P(m\text{-}C_6H_4SO_3Na)]$	unsaturated aldehydes	[68]
Ru(II), Rh(I), Ir(I) with $Ph_2P(m\text{-}C_6H_4SO_3Na)$, $HRu(O_2CH)$-$[Ph_2P(m\text{-}C_6H_4SO_3Na)]$ etc.	selective reduction of aromatic and aliphatic aldehydes	[69]
Pt complexes/$Ph_2P(m\text{-}C_6H_4SO_3Na)$	aromatic aldehydes	[138]
Hydrogenation of CO_2		
$[Rh(NBD)(PMe_2Ph)_3]BF_4$	hydrogenation of CO_2 to formic acid	[139]
$RuH_2(CO)(PPh_3)_3$	CO_2 to HCOOH ($CO_2/H_2/H_2O$)	[140]

and PTA could also be prepared in high yield from tris(hydroxymethyl)phosphine and hexamethylenetetramine. This complex would thus be useful for this type of reaction.

Basset and coworkers reported hydrogenation of propionaldehyde in water catalyzed by $[RuCl_2(TPPTS)_3]$, $[HRuCl(TPPTS)_2]$, $[HRu(OAc)(TPPTS)_3]$ or $[RuH_2(TPPTS)_4]$ [51–53]. The catalytic hydrogenation proceeded at 100°C even without sodium iodide (Table 8). Similar catalytic activities were observed for this reaction not only in water but also in the classic solvents (chlorobenzene, dioxane etc.), although the extremely low activities were observed at room temperature. However, the reaction rates were significantly enhanced upon addition of NaI in water, and propionaldehyde was thus efficiently hydrogenated under mild conditions (35°C, Table 9). Active species would be $[HRuI(TPPTS)_2]$ which was formed by metathesis of the chlororuthenium species with NaI. NaI would also assist the formation of a metal–carbon bond from propionaldehyde to give

Table 8
Solvent influence on the hydrogenation of propionaldehyde

Catalyst precursor	Solvent	First order rate constants k (h^{-1})
$1/2[RuCl_2(TPPTS)_2]_2$ + TPPTS	H_2O	0.83
$RuCl_2(PPh_3)_3$	C_6H_5Cl	0.86
	dioxane	1.8
	THF	1.7
$RuHCl(TPPTS)_3$	H_2O	0.69
$RuHCl(PPh_3)_3$	C_6H_5Cl	0.80
	dioxane	1.6
	THF	1.5

Reaction conditions: [EtCHO] = 0.8 M, [Ru] = 0.8 mM, solvent 60 ml, 100°C, 50 bar H_2 (at 25°C).

Table 9
Propionaldehyde hydrogenation in the presence of water-soluble complexes: Influence of sodium iodide on the reaction rate

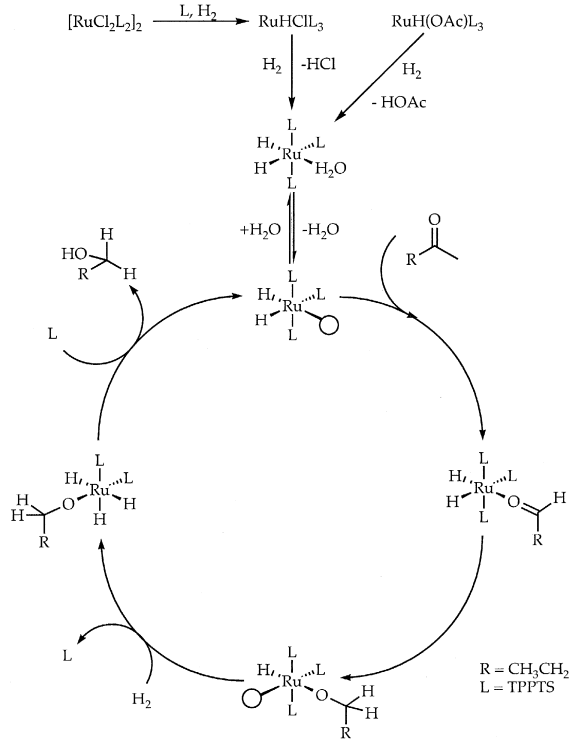
Catalyst precursor	Initial reaction rate [a]	
	without NaI	with NaI
$1/2[RuCl_2(TPPTS)_2]_2 + TPPTS$	0	2000
$RuCl_2(TPPTS)_3$	0	2200
$RuH(OAc)(TPPTS)_3$	0	2100
$RuH_2(TPPTS)_3$	0	2350
$RuHI(TPPTS)_3$	0	2020
$[Ru(CO)_2(OAc)(TPPTS)]_2$	0	0

Reaction conditions: [EtCHO] = 0.8 M, [Ru] = 0.8 mM, H_2O 60 ml, 35°C, 50 bar H_2.
[a] Initial reaction rate = (mol propanol) × (mol Ru)$^{-1}$ × h^{-1}

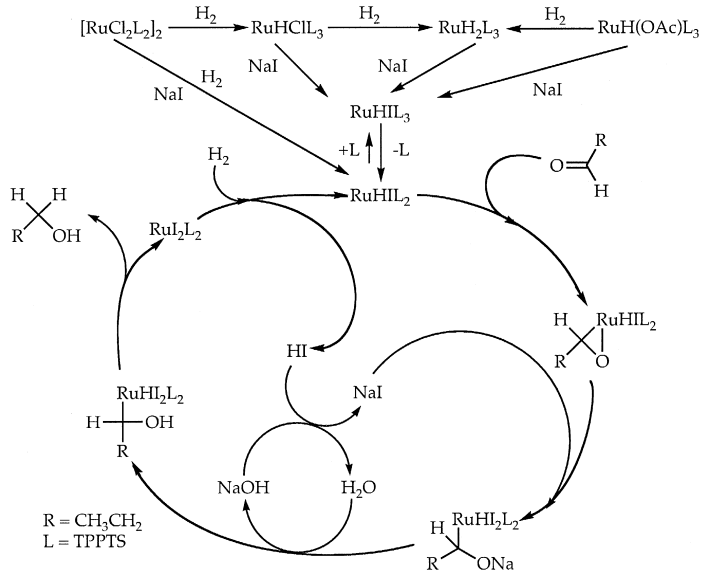
the intermediate RuCH(Et)ONa which reacts with water to give a RuCH(OH)Et species. They proposed that the reaction mechanism in the presence of NaI (Scheme 2) was different from that in the absence of NaI (Scheme 1), and attempted to explain the role of sodium iodide on this reaction.

2.2.1. Selective reduction of the carbonyl group of α,β-unsaturated carbonyl compounds

As shown above, a lot of reports for selective the hydrogenation of the carbon–carbon double bond of α,β-unsaturated carbonyl compounds have already been published [54–58]. Generally, transition metal catalyzed hydrogenation of olefins is readily achieved under mild conditions with high selectivity, whereas the catalytic reduction of the aldehyde remains a challenging problem. The most popular selective reducing method is a stoichiometric reduction with various metal hydride reagents (mainly boron and aluminum hydrides) [59,60], and the Meerwein–Pondorf–Verley type reduction of



Scheme 1.



Scheme 2.

the carbonyl group catalyzed by group IVA metals [61] or transition metal catalysts [62–66] have been used. Transition metal catalyzed hydrosilylaton has been described as an efficient method, however this type of reaction accompanies a stoichiometric amount of by-product derived from silane. Chemoselective hydrogenation of carbonyl groups by transition metal catalysts is by far the most attractive way to carry out the reduction concerning economical and industrial process considerations.

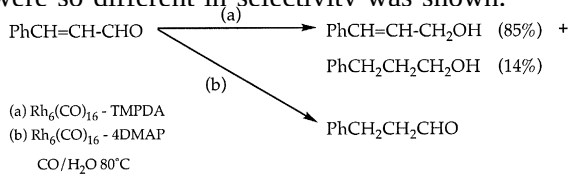
Kaneda et al. showed that effective amines were different for selective hydrogenation of the C=C double bond or C=O bond of α,β-unsaturated aldehyde by $Rh_6(CO)_{16}$ under CO/H_2O conditions (Eq. (4)) [67]. In these catalytic reactions, TMPDA (N,N,N',N'-tetramethyl-1,3-propanediamine) was

Table 10
Hydrogen transfer reduction of aldehydes by $RuCl_2(TPPMS)_2$

Substrates	Time (h)	Conv. (%)	Yield (%)
Ph–CHO	1.5	99.7	94
4-Me–C_6H_4–CHO	1.5	99.5	99
4-OMe–C_6H_4–CHO	1.5	98.8	90
4-Br–C_6H_4–CHO	1.5	99.8	94
2,6-$Cl_2C_6H_3$–CHO	1.5	100	96
3,4,5-$(OMe)_3C_6H_2$–CHO	8	98.6	91
4-$Me_2NC_6H_4$–CHO	1.5	98.9	98
2-NO_2–C_6H_4–CHO	2	100	90
Ph–CH=CH–CHO	2	98	92
CH_3–CH=CH–CHO [a]	2.5	—	78
Me_2C=$CHCH_2CH_2$CMe=CH–CHO [b]	7	98	95
Me_2C=$CHCH_2CH_2$CHMeCH_2–CHO	4	93	90
2-naphthaldehyde	3.5	100	98
Pyrrole-2-carboxaldehyde	5	99.8	66
2-OH-1-naphthaldehyde	3	0	98 [c]
2-OH–C_6H_4–CHO	3	0	63 [c]

Reaction conditions: $RuCl_2(TPPMS)_2$ 0.01 mmol, TPPMS 0.1 mmol, aldehyde 1 mmol, 5 M HCOONa aqueous solution 3 ml, 80°C.
[a] 30°C, side reactions at 80°C.
[b] Mixture of geranial and neral (2:1). No isomerization was observed.
[c] Only the starting material could be recovered.

effective for the selective reduction of aldehyde, whereas 4-DMAP (4,4-dimethylaminopyridine) was effective for the selective hydrogenation of olefins. However, as far as we know, no convincing reason why these amines were so different in selectivitv was shown.

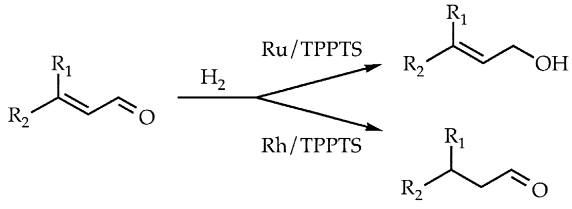


(4)

Joo and Benyei reported that unsaturated olefins such as cinnamaldehyde, crotonaldehyde, 1-citronellal, and citral could be reduced to unsaturated alcohols under mild conditions (30–80°C) [68,69]. The C=O group was reduced exclusively by hydrogen transfer from $HCOONa/H_2O$ catalyzed by $RuCl_2(TPPMS)_2$ with the TPPMS system (Eq. (5)). As shown in Table 10, neither hydrogenation nor hydrogenolysis of substituents on the aromatic rings was observed. A strongly coordinating substituent *ortho* to the aldehyde group inhibits the reaction completely. They also studied the reduction of benzaldehyde catalyzed by various transition metal complexes coordinated with TPPMS in water (conditions: 80°C, with 10 equiv. of TPPMS), and showed that $RhCl(TPPMS)_3$ was much less active than $RuCl_2(TPPMS)_2$, $HRuCl(CO)(TPPMS)_3$. $IrCl(CO(TPPMS)_2$ showed low catalytic activity, and lost its catalytic activity in less than 10 min under the same conditions.

$$RCH{=}CHCHO \xrightarrow[HCOONa/H_2O,30-80°C]{RuCl_2(TPPMS)+TPPMS} RCH{=}CHCH_2OH \quad (5)$$

Mercier et al. at Rhone-Poulenc reported selective hydrogenation of α,β-unsaturated aldehydes (important intermediates for vitamins, flavor and fragrance chemicals) to the corresponding allylic alcohols in water. They showed that the Ru/TPPTS catalyst was very effective in a two phase system, because the reaction proceeded at quantitative conversions with exclusive selectivity of the C=O group under mild reaction conditions [70–73]. These results are in sharp contrast to those of the corresponding rhodium complexes which catalyze the selective hydrogenation of α,β-unsaturated aldehydes to the saturated aldehydes (Scheme 3, Table 11) [73]. Hydrogenation of 3-methyl-2-buten-1-al to 3-methyl-2-buten-1-ol, for example, proceeded with 100% conversion and 97% selectivity at 35°C, 20 bar of H_2 pressure and 1 h reaction time in an aqueous/organic (1/1) system. Various effects such as hydrogen pressure, ruthenium or substrate concentration, temperature, stirring rate, and ligand concentration on hydrogenation of 3-methyl-2-buten-1-al catalyzed by $RuCl_3$–TPPTS system were examined. No significant change of the 3-methyl-2-buten-1-ol selectivity was however observed by varying hydrogen pressure, ligand concentration, or stirring rate (> 1500 rpm). The 3-methyl-2-buten-1-ol selectivity decreased slightly at > 50°C and 3-methylbutan-1-ol was also formed as the totally hydrogenated product, although raising the temperature would be beneficial for the catalytic activity (Table 12). The catalyst could be recycled without loss of selectivity. Analysis of the ruthenium, phosphorus, and sulfur species in both phases proved no leak of metal and TPPTS into the



Scheme 3.

Table 11
Hydrogenation of α,β-unsaturated aldehydes with Ru- or Rh–TPPTS catalysts [73]

Metal	Substrate	P_{H_2} bar	Temp. (°C)	Time (h)	Conv. (%)	Selectivity (%)	
						alcohol [a]	aldehyde [b]
Rh	3-phenyl-2-propenal	20	80	1.5	93	—	95.7
Ru	3-phenyl-2-propenal	20	35	3	99	98	—
Rh	3-methyl-2-butenal	20	80	0.3	90	—	95
Ru	3-methyl-2-butenal	20	35	1	100	97	—
Rh	3,7-dimethyl-2,6-octenal	40	60	3	19	—	95
Ru	3,7-dimethyl-2,6-octenal	50	50	15	96	98	—

Reaction conditions: $[RhCl(COD)]_2$ 0.05 mmol or $RuCl_3$ 0.1 mmol, TPPTS 0.5 mmol, substrates 20 mmol,water/toluene = 5/5 ml.
[a] Unsaturated alcohols hydrogenated C=O.
[b] Unsaturated aldehydes hydrogenated C=C.

organic phase. Addition of buffers to maintain neutral pH conditions inhibited the hydrogenation of the C=C double bond that was favored in an acidic medium. Similar studies for the hydrogenation of α,β-unsaturated aldehydes (cinnamaldehyde) using other ruthenium complexes such as $[RuCl(\mu\text{-}Cl)(TPPTS)_2]_2$, $RuHCl(TPPTS)_3$, $RuH_2(TPPTS)_4$ [39] or osmium–TPPTS complexes [74] have been explored recently by other researchers.

NMR studies of the complex $HRu(TPPTS)_3$ in the presence of hydrogen have demonstrated an equilibrium between mono- and dihydride species [73]. This pathway might involve the dihydride complex (or its tautomeric η^2-H_2 complex) as a catalytic intermediate. They proposed a plausible mechanism involving (i) coordination of an aldehyde to a low-valent coordinatively unsaturated hydrido-Ru(II) complex, (ii) hydride transfer to a coordinated aldehyde to form either a metal–alkoxy or metal–hydroxyalkyl intermediate, (iii) oxidative addition of molecular hydrogen, and (iv) reductive elimination of alcohol (Scheme 4). Since this pathway might involve the dihydrido complex as a catalytic intermediate, oxidative addition of H_2 to an electron-rich Ru(0)–TPPTS complex should therefore take place prior to aldehyde coordination. The reaction mechanism remains speculative, and the study is still in progress.

2.3. Asymmetric hydrogenation of prochiral olefins

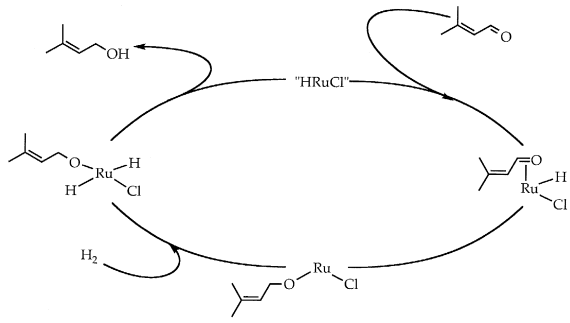
Among a lot of applications of homogeneous catalysis in water to organic reactions, the synthesis of chiral compounds by asymmetric hydrogenation or reduction of C=C or C=O bonds is one of the most fascinating goals in this research field. Although a lot of successful examples have been reported especially for selective catalytic hydrogenation using transition metal complexes [75], the following problems pointed out by Davis might still remain [76].

(1) The catalyst species can be very expensive (e.g., rhodium–phosphine complex).

Table 12
Influence of reaction temperature for hydrogenation of 3-methyl-2-butenal by $RuCl_3$–TPPTS catalyst [73]

Temp. (°C)	Time (min)	Conv. (%)	Yield (%) of	
			3-methyl-2-butenol	3-methylbutanol
35	100	97	96	—
50	50	100	99	—
80	25	98	93	4
100	25	100	92	6

Reaction conditions: $RuCl_3$/TPPTS = 0.5/18 mmol, buffer (pH = 7) 100 ml, 3-methyl-2-butenal 0.5 mmol, H_2 20 bar. Prereduction: H_2 20 bar, 50°C, 1 h.

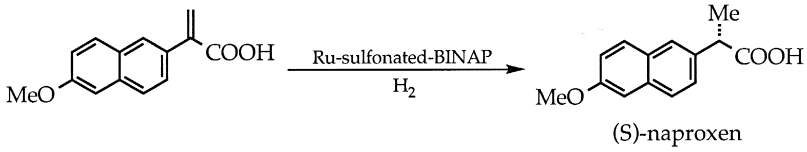


Scheme 4.

(2) The catalytic species may not survive during a separation process and/or the separation may not be as complete or cost-effective as desired.

(3) Catalyst contamination in pharmaceutical products must be minimized.

Wan and Davis recently reported modified SAP (Supported Aqueous Phase) catalysts consisting of ruthenium-sulfonated-BINAP and CPG-240 (CPG: Controlled Pore Glass) were remarkably effective for asymmetric hydrogenation of 2-(6′-methoxy-2′-naphthyl)acrylic acid affording naproxen (Eq. (6)) [77].



(6)

In their earlier work [76], they reported 96% ee for the hydrogenation of 2-(6′-methoxy-2′-naphthyl)acrylic acid by [Ru(benzene)(BINAP–$4SO_3Na$) in methanol. However, the reaction rate of the two-phase system (solvent: methanol–water) was at least 350 times slower than that of the homogeneous reaction system (solvent: methanol only), due to the limited solubility of this substrate in water. The reaction thus took place at the interface of the aqueous–organic phase. A controlled pore glass (CPG-240) supported SAP–Ru–BINAP–$4SO_3Na$ catalyst system was examined for this reaction in ethyl acetate, but showed low ee (up to 70% ee). However, they greatly improved the catalyst system that consisted of a thin film of [Ru(BINAP–$4SO_3Na$)(benzene)Cl]Cl and ethylene glycol on a controlled pore glass, and the desired product (96% ee) could be obtained at 100% conversions of the substrate (H_2 94–101 MPa, 276 K, solvent 1:1 mixture of chloroform–cyclohexane) [77]. In addition, the reaction rate of the heterogeneous system was higher than that of the homogeneous system. The SAP catalyst was easily recycled without any leaching of ruthenium into the organic phase.

3. Efficient selective reduction of aromatic nitro compounds under CO/H_2O conditions

3.1. Introduction: Conventional selective reduction of aromatic nitro compounds

Generally, aromatic amines have been practically produced from the corresponding nitro compounds by (1) stoichiometric reduction using iron powder, or metal sulfides such as alkali metal sulfides and alkali metal hydrogen sulfides like NaHS, and/or (2) catalytic hydrogenation with palladium–, and platinum–carbon, and Raney-nickel etc. However, some difficulties such as (1) the problem of after-treatments of the by-products, or (2) loss of the selectivity toward the desired

Table 13
Examples for the catalytic reduction of aromatic nitro compounds under CO/H_2O conditions

Catalysts	Substrates, comments etc.	Ref.
$Rh_6(CO)_{16}$ / *N*-methylpyrrolidine etc.	nitrobenzene etc., 50–150°C/ CO 50–120 atm	[83,84]
$Rh_6(CO)_{16}$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Ir_4(CO)_{12}$ etc/ NMe_3 aqueous solution	nitrobenzene, dinitrotoluene, 100–180°C, CO 500 psi	[85]
$Rh_6(CO)_{16}$ / *N*,*N*-dimethylbenzylamine	nitrobenzene, 100–120°C, 350 psi, Reduction by $H_2/CO/H_2O$, H_2/H_2O or CO/H_2O	[86]
$Ru_3(CO)_{12}$ / $PhCH_2N(C_2H_5)_3^+ Cl^-$ /NaOH aq.	nitrobenzene etc., CO 1 atm, r.t.	[96]
$Ir_4(CO)_{12}$, $Rh_6(CO)_{12}$ / NMe_3 aq.	nitrobenzene, dinitrobenzene etc., $CO/H_2/H_2O$, 92–187°C	[141]
Se/NEt_3	4-$RC_6H_4NO_2$ (R = H, OMe, Cl, Br, Me)	[142]
$Rh_6(CO)_{16}$ /substituted pyridines, TMEDA etc.	nitrobenzene, CO 700 mmHg, 80°C	[87]
$[Ru(COD)py_4](BPh_4)_2$ etc. py = pyridine	nitrobenzene, CO 50 atm, 145°C	[90]
$[Co(teten)](ClO_4)_2 \cdot 2H_2O$, teten = 2,3,9,10-tetraethyl-1,4,8,11-tetraaza-1,3,8,10-cyclotetradecaene	reduction of aliphatic, aromatic, heterocyclic nitro compounds	[143]
$PtCl_2(PPh_3)_4/SnCl_4/NEt_3$	nitrobenzenes, CO 60 atm, 80°C	[88,89]
Fe oxide on alumina/Cs, Rb	nitrobenzene, CO 1 atm, 300–350°C	[144]
$Rh_6(CO)_{16}$ / 3,4,5,6,7,8-Me_6phen etc., phen = phenanthroline	nitrobenzene, CO 30 atm, 165°C	[91–94]
$Co_2(CO)_8$-[1,5-HDRhCl]$_2$ / *n*-$C_{12}H_{25}N(CH_3)_3^+ Cl^-$ /NaOH aq., 1,5-HD = 1,5-hexadiene	nitrobenzene, CO 1 atm, r.t.	[98,99]
$Co(CO)_8$ /MeI or $PhCCo_3(CO)_9$, CTAB/NaOH aq., CTAB = cetyltrimethylammonium bromide	nitrobenzene, CO 1 atm, r.t.	[100]
$CpV(CO)_4$ / $nBu_4N^+ HSO_4^-$ /NaOH aq.	$ArNO_2$, α,β-unsaturated aldehydes	[101]
(η^4-$Ph_4C_4C{=}O)(CO)_3Ru$	$ArNO_2$, CO 500 psi, 108°C	[108]
$Rh(CO)_2(acac)$, $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Ru_3(CO)_{12}$ /amines, phosphines/NaOH aq.	$ArNO_2$, CO 1 atm, r.t.–50°C	[97,102–106]
$Ru_3(CO)_{12}$ /amines	$ArNO_2$, CO 20–50 atm, 120–180°C	[110–112]
$Ru_3(CO)_{12}$ /DIAN–R, R = Me, Cl, OMe	nitrobenzene, CO 30 bar, 150–180°C	[113]
$K[Rh(CO)_4]$, $PPN[Rh(CO)_4]$ etc.	nitrobenzene, CO 40–80 atm, 200°C	[95]
$Rh_6(CO)_{16}$ /TMPDA or aminated polystyrene	$ArNO_2$, CO 2–8 atm, 80°C	[114]
Palladium/TPPTS or BINAS, BINAS = mixture of tetra-, penta-, hexa-sulfonated 2,2-bisdiphenylphosphinomethylene binaphthyl	$ArNO_2$, CO 60–80 bar, 50–100°C	[115]

amines, still remain. The efficient specific catalytic reduction of aromatic nitro compounds is thus an especially attractive subject from both synthetic and practical viewpoint, because the desired amine can be catalytically obtained as a sole product, and the above-mentioned problems might be improved.

From the aspect of industrial utilization of carbon monoxide, the water-gas shift reaction (WGSR, Eq. (7)) has been one of the most important processes (for example (Review) [78,79]); it has already been commercialized to produce pure hydrogen.

$$CO + H_2O \rightarrow H_2 + CO_2 \quad (7)$$

The studies concerning the reduction of aromatic nitro compounds under CO/H_2O conditions using homogeneous catalysts (Eq. (8)), have thus been reported (for previous reviews see Refs. [80–82]). As mentioned above, the great importance of this catalytic reaction should be emphasized, if the reaction can be performed in an efficient manner. This process might be especially useful from industrial viewpoints, because the catalytic process with CO and water might introduce a new possibility to accomplish the chemoselective reduction due to the unique reducing source different from dihydrogen.

$$ArNO_2 + 3CO + H_2O \rightarrow ArNH_2 + 3CO_2 \quad (8)$$

In Section 3.2, the author would like to summarize the previous results for the reduction of aromatic nitro compounds with CO and water. From these results and previous comments, the author would also like to attempt to understand the reaction pathways in detail. The author also presents our recent results and applications for this catalytic process.

Table 14
Effect of various amines as additives on the reduction of nitrobenzene and the water–gas-shift reaction (WGSR) [87]

Amines (pKa)		Reduction[a]		WGSR[b]
		Time (h)	$PhNO_2$ Conv.	Activity[c]
$H_2N(CH_2)_2NH_2$	(9.97)	10	34	75
$H_2N(CH_2)_3NH_2$	(10.84)	10	45	32
$Me_2N(CH_2)_2NMe_2$	(8.97)	4	100	2.5
$Me_2N(CH_2)_3NMe_2$	(10.2)	2.5	100	0
	(6.75)	10	80	0
	(9.17)	1.4	100	3.7
	(9.70)	1.4	100	2.8
	(10.1)	5	92	2.3

[a] $PhNO_2$ 1.5 mmol, $Rh_6(CO)_{16}$ 0.05 mmol, H_2O 40 mmol, amine 15 mmol, 2-ethoxyethanol [3-(volume of amine)] ml, 80°C, CO 700 mmHg.
[b] $Rh_6(CO)_{16}$ 0.05 mmol, H_2O 40 mmol, amine 85 mmol, 2-ethoxyethanol [10-(volume of amine)] ml, 100°C, 4 h.
[c] Turnover number = mol hydrogen/mol rhodium complex per 4 h.

3.2. Catalytic reduction of aromatic nitro compounds under CO/H_2O conditions

Table 13 summarizes some examples for the catalytic reduction of aromatic nitro compounds under CO/H_2O conditions. The reductions catalyzed by $Rh_6(CO)_{16}$ in the presence of *N*-methylpyrrolidine [83,84], NMe_3 [85], *N*,*N*-dimethylbenzylamine [86], *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine (TMPDA) [87], γ-dimethylaminopyridine (4-DMAP) [87] are the pioneer works in this research field. Various transition metal–carbonyl complexes such as $Fe(CO)_5$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Ir_4(CO)_{12}$ were revealed to exhibit the activity for nitrobenzene in the presence of trimethylamine at the same period [85]. Among this early work, Kaneda reported an interesting observation that effective amine additives are quite different between the WGSR and in the reduction of nitrobenzene (Table 14) [87]. TMPDA and 4-DMAP are the most effective additives in their catalytic reactions. No convincing correlation between the selectivity and the basicity nor the steric hindrance of the amines was proposed. The reduction using $PtCl_2(PPh_3)_2$–$SnCl_4$–Et_3N [85,86], or $[Ru(COD)py_4](BPh_4)_2$ (COD = 1,5-cyclooctadiene, py = pyridine) [90] was also reported at the same period.

Alessio et al. showed that the same $Rh_6(CO)_{16}$ complex was also very effective for the catalytic reduction of nitrobenzene in the presence of substituted phenanthrolines [91–94], in particular 3,4,5,6,7,8-Me_6phen (HMphen, phen = phenanthroline, Table 15). The catalytic activity exhibited by $Rh_6(CO)_{16}$ + chel system (chel: HMphen etc.) strongly depended on the nature (chelating power) of the ligands. The reaction rate using $Ru_3(CO)_{12}$ was also enhanced upon addition of HMphen. The main role of the chelating ligand would be coordination to a mononuclear fragment [Rh(chel)], probably because $Rh_6(CO)_{16}$ + chel and a mononuclear Rh(I) cationic complex such as $[Rh(chel)(CO)_2]$ showed comparable activities. The activity of the system also strongly depended on the chel/Rh molar ratio and the reaction temperature due to the change of the fragmentation equilibrium between the polynuclear and mononuclear species.

More recently, Ragaini and Cenini have reported that $[Rh(CO)_4]^-$ (either as a K^+, Cs^+ or PPN^+ salt, $PPN = (PPh_3)_2N^+$) was a very active catalyst for the reduction of nitrobenzene without adding a ligand [95]. Metal salts of $[Rh(CO)_4]^-$ are water soluble, easily prepared in one step in virtually quantitative yields from $RhCl_3$. The conversion of nitrobenzene was markedly increased upon the addition of $PhCH_2(C_2H_5)_3N^+Cl^-$ as a phase-transfer agent. Addition of an inorganic base showed a negative effect: the scope and limitation of the catalysis will be introduced in the near future.

The reduction of aromatic nitro compounds by $Ru_3(CO)_{12}$ in the presence of an alkaline aqueous solution, such as NaOH, reported by Alper et al. was also one of the pioneer works in this field [96], because the reaction took place under the extremely mild reaction conditions: atmospheric pressure of carbon monoxide at room temperature. The base concentration was found to be very important to perform the efficient catalytic activity, as also demonstrated by our report using the rhodium–dppe

Table 15
Reduction of nitrobenzene with CO and H_2O in the presence of $rh_6(co)_{16}$ + chelate amines as catalyst precursors [91–94]

Chelate amines (pK_a)	Amine/Rh molar ratio	Aniline conv. after 2 h
Pyridine (5.25)	2	0
Bipy (4.44)	1	0.8
4,4′-Me_2bipy (5.32)	1	3.0
Phen (4.93)	1	7.5
4,7-Me_2phen (5.95)	1	25
3,4,7,8-Me_4phen (6.31)	1	53
3,4,5,6,7,8-Me_6phen (7)	1	73

Conditions: 0.83×10^{-6} mol of $Rh_6(CO)_{16}$, EtOH (95%) 50 ml, CO 30 atm, 165°C, 2 h.

Table 16
Reduction of nitrobenzene catalyzed by $Rh(CO)_2(acac)$ complexes under CO/H_2O conditions — Effect of amine additives — [106]

Amine	Molar ratio [a]	Turnovers [b]
None [c]	—	< 1
None	—	37
$H_2N(CH_2)_2NH_2$	1.5	52
$Me_2N(CH_2)_2NMe_2$	1.5	68
o-Phenylenediamine	1.5	155
2,3-Diaminonaphthalene	1.5	99
9,10-Diaminophenanthrene	1.5	122
9,10-Diaminophenanthrene	1.5	172 [d]
1,8-Diaminonaphthalene	1.5	68
Pyridine	3.0	61
NEt_3	3.0	66

Reaction conditions: 2-methoxyethanol/ 5 N NaOH aq. = 15/5 ml, $Rh(CO)_2(acac)$ 0.02 mmol, $PhNO_2$ 5 mmol, 25°C, CO 1 atm, 3 h.
[a] Molar ratio of amine/Rh.
[b] Turnovers = amount of aniline formed (mmol)/ Rh (mmol).
[c] H_2O (5 ml) was used in stead of 5 N NaOH aq.
[d] $Rh(CO)_2(acac)$ 0.01 mmol.

(dppe = $Ph_2P(CH_2)_2PPh_2$) catalyst system [97]. The active catalytic species would be metal carbonyl hydride anions, formed by attack of the hydroxide ion at a coordinated CO followed by elimination of carbon dioxide, as shown in Eq. (9).

$$Ru_3(CO)_{12} + R_4NOH \rightarrow R_4N^+\left[Ru_3(CO)_{11}(CO_2H)\right]^- \underset{-CO_2}{\rightarrow} R_4N^+\left[HRu_3(CO)_{11}\right]^- \quad (9)$$

Various transition metal complexes such as $Co_2(CO)_8/[(1,5\text{-HD})RhCl]_2$ (1,5-HD = 1,5-hexadiene) [98,99], $Co_2(CO)_8$/MeI or $Ph_3CCo_3(CO)_9$ [100], $CpV(CO)_4$ [101], were thus examined as the catalyst precursors for the reduction under the above-mentioned mild reaction conditions in the presence of NaOH aqueous solution.

We recently reported that homogeneous catalyst systems, composed of rhodium–carbonyl complexes and prescribed amines or *tert*-phosphines in the presence of NaOH aqueous solutions, exhibited remarkably high catalytic activities for the reduction of aromatic nitro compounds even under the mild conditions of room temperature and 1 atm of CO [97,102–106]. The activities were markedly increased in the presence of amine and/or phosphine additives. 9,10-Diaminophenanthrene was especially effective, as the results of huge amount of catalyst screening for the reduction of $PhNO_2$ using $Rh(CO)_2(acac)$ (37 → 127 turnovers, Table 16): other amines such as *o*-phenylenediamine, triethylamine etc. were also especially favorable [103]. The most effective amine additive however, was found to be dependent upon the rhodium species used, and/or upon the substrates. The reason why these amines are so especially effective is not clear at this moment. We also reported that the reduction of $PhNO_2$ using $Rh(CO)_2(acac)$–PEt_3 or PEt_2Ph proceeded at significant rates: the activity was markedly increased at higher reaction temperature in glyme (glyme: diethyleneglycol dimethyl ether) solvent (Table 17) and/or higher CO atmosphere [104]. Both electronic and steric factors of *tert*-phosphine used play an important role in exhibiting the high catalytic activities.

During the study of these catalyses, we observed the interesting fact that only the aromatic nitro group was reduced affording the corresponding amines in high yields. These results are very important especially from our practical viewpoints. However, the formation of a by-product, Na_2CO_3 from CO_2 and NaOH, in these catalytic reactions might be a practical concern for this process.

As described above, it has been well-known that NMe_3-added $Ru_3(CO)_{12}$ showed notable catalytic activity for the reduction of nitrobenzene with CO (500 psi) and H_2O in THF (100°C) [85]. A very

Table 17
Reduction of nitrobenzene catalyzed by phosphine-added $Rh(CO)_2(acac)$ complexes under CO/H_2O conditions [104]

Phosphine	δOPR_3 [a]	Cone angle [b]	P/Rh	Temp. (°C)	Turnovers
None	—	—	—	25	5
PPh_3	−27	145	1	25	7
$PEtPh_2$	−33	140	1	25	14
PEt_2Ph	−42	136	1	25	116
PEt_2Ph	−42	136	1	50 [c]	609
PEt_3	−48	132	1	25	241
PEt_3	−48	132	2	25	154
PEt_3	−48	132	1	50 [c,d]	861
PCy_3	−50	170	1	25	35
$P(i\text{-}Pr)_3$	−55	160	1	25	27
$P(OEt)_3$	+1	109	1	25	21
$P(OPh)_3$	+18	128	1	25	39

Reaction conditions: $Rh(CO)_2(acac)$ 0.005 mmol; diglyme/5 N NaOH aq. = 7.5/2.5 ml; $PhNO_2$ ca. 5 mmol; CO 1 atm; 2 h.
[a] ppm.
[b] θ.
[c] Diglyme/5 N NaOH aq. = 15/5 ml.
[d] $Rh(CO)_2(acac)$ 0.001 mmol.
diglyme = diethyleneglycol dimethyl ether.

large amount of dihydrogen (52% H_2 in gas phase after 2 h) was produced as a by-product, because this catalyst system is also exceptionally active for the water–gas shift reaction [107], as shown in Table 18. Therefore, the reduction by this catalyst seemed to proceed by hydrogenation of nitrobenzene with dihydrogen which was formed by the WGSR.

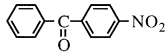
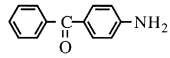
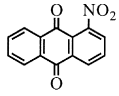
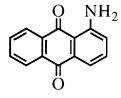
In contrast, Kiji et al. reported the interesting observation that $[Ru(cod)py_4](BF_4)_2$ which was also effective for the reduction of nitroarenes (slov. THF) possessed no catalytic activity for the WGSR [90]. Shvo et al. also reported that $(\eta^4\text{-}Ph_4C_4C{=}O)Ru(CO)_3$ showed catalytic activity for the reduction of aromatic nitro compounds under CO/H_2O, but showed no activity under H_2 [108]. A comparative study using Ru(II) complexes for the reduction of $PhNO_2$ under H_2, CO/H_2 or CO/H_2O conditions was also attempted by Sanchez-Delgado et al. [109].

As the results of huge amounts of screening of additives for the reduction of nitrobenzene with CO/H_2O, ruthenium–carbonyl compounds in the presence of a prescribed small amount of amines such as NEt_3, $HN(i\text{-}Pr)_2$, $HNEt_2$, $HN(cyclohexyl)_2$, pyrrolidine, or piperidine were found to be especially effective [110–112]. The activities were also remarkably increased at higher reaction temperatures under higher CO pressures. The product from nitrobenzene sometimes contained a trace amount of azoxybenzene and azobenzene, however they were eventually converted to aniline by further stirring as previously mentioned by Shvo et al. [108]. Both the catalytic activity and selectivity of aniline in these catalysts were strongly dependent upon the molar ratio of additive to ruthenium,

Table 18
The water–gas shift reaction by amine-promoted ruthenium catalysts [107]. Effect of amine additives

Catalyst	Solvent/amine	CO (atm)	Temp. (°C)	Turnovers after 10 h
$Ru_3(CO)_{12}$	diglyme/Me_3N	51	100	5740
$Ru_3(CO)_{12}$	diglyme/Et_3N	51	100	860
$Ru_3(CO)_{12}$	diglyme/Bu_3N	51	100	540
$Ru_3(CO)_{12}$	diglyme/pyridine	51	100	300
$Ru_3(CO)_{12}$	diglyme/$HNMe_2$	51	100	2200

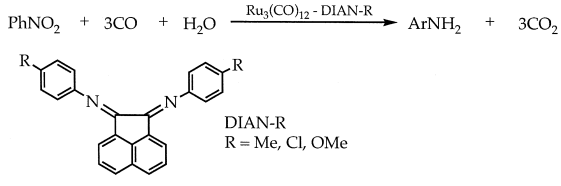
Table 19
Exclusive reduction of aromatic nitro compounds with CO and water catalyzed by $Ru_3(CO)_{12}$–HN(*i*-Pr)$_2$ [110]

$ArNO_2$	$ArNH_2$	Yield / %
		>99
		>99
		>99
		>99
		>99

$Ru_3(CO)_{12}$ /HN(*i*-Pr)$_2$ or NEt_3, CO 20 atm, 150°C.
Diglyme (diethyleneglycol dimethyl ether) – H_2O solvent.

solvent/water ratio, sometimes upon solvent. The optimization of the reaction conditions is thus required to obtain the best result.

Ragaini and Cenini et al. have recently reported that Me–DIAN was an especially effective additive for the reduction of $PhNO_2$ (Eq. (10)) by $Ru_3(CO)_{12}$ [113]. They also attempted a comparison of effective promoters (such as NEt_3, 9,10-diaminophenanthrene, substituted phenanthrolines etc.) previously reported, but it seemed difficult to compare those under the same reaction conditions.



(10)

3.2.1. Selective catalytic reduction of aromatic nitro compounds by homogeneous catalysts under CO / H_2O conditions

It should be noted that the reductions by $Ru_3(CO)_{12}$–HN(*i*-Pr)$_2$ or NEt_3 catalysts proceeded with exclusive selectivity toward aromatic nitro-group (almost 100%) [110–112], resulting in the formation of the desired aromatic amines in high yields (Table 19). The selectivities of the nitro-group did not change irrespective of the kind of these amines (HN(*i*-Pr)$_2$, NEt_3, and piperidine). *p*-Cyanonitrobenzene, *p*-nitrobenzophenone and 1-nitroanthraquinone were converted to the corresponding *p*-aminobenzonitrile, *p*-aminobenzophenone and 1-aminoanthraquinone, respectively, without reduction of C=O, C≡N. As far as we know, previous patents [84,93] and papers disclosed that aromatic nitro compounds optionally substituted by an inert group such as alkyl, alkoxyl were effective for this type of reduction by rhodium or ruthenium catalysts. Therefore, we believe, these results are very important from both synthetic and industrial viewpoints.

Table 20
Reaction of various substrates under CO/H_2O conditions

Substrate	Amine	Product	Yield (%)
$PhNO_2$	$HN(i\text{-}Pr)_2$	$PhNH_2$	> 99%
$PhNO_2$	NEt_3	$PhNH_2$	> 99%
$PhCOCH_3$	$HN(i\text{-}Pr)_2$	no reaction [a]	
$PhCOCH_3$	NEt_3	no reaction [a]	
PhC≡CH	$HN(i\text{-}Pr)_2$	no reaction [a]	
PhC≡CH	NEt_3	$PhCH{=}CH_2$	1.3%
$PhCH{=}CH_2$	NEt_3	$PhCH_2CH_3$	0.3%
PhCHO	NEt_3	$PhCH_2OH$	0.08%
PhC≡N	$HN(i\text{-}Pr)_2$	no reaction [a]	

Reaction conditions: $Ru_3(CO)_{12}$ /amine = 0.01/1.5 mmol, diglyme/H_2O = 15/5 ml, CO 20 atm, 150°C, 2 h, substrate 5 mmol.
[a] Trace amount of product (< 0.05%) might be detected on GC chromatogram.

Noteworthy was that other substrates such as acetophenone, phenylacetylene, and benzonitrile, styrene, and benzaldehyde were not reduced under the same reaction conditions ($Ru_3(CO)_{12}$–NEt_3 or $HN(i\text{-}Pr)_2$), as exemplified in Table 20. The potential importance of these catalysts could be emphasized, because the desired aromatic amines could be obtained in high yields. In addition, a stoichiometric amount of CO_2 was formed at the end of the reduction; hydrogen gas was not formed by these catalytic reactions (Table 21). A trace amount of hydrogen gas was detected for benzonitrile under the same conditions.

As shown in Tables 19 and 21, the above mentioned catalyst systems were very effective for the exclusive reduction of 1-nitroanthraquinone affording 1-aminoanthraquinone in high yields [110–112]. The effect of amine additives and cocatalysts for the reaction was explored: rhodium–carbonyl complexes such as $Rh_4(CO)_{12}$ in the presence of certain amines also showed high selectivity of aromatic nitro-groups for the reduction of 1-nitroanthraquinone affording 1-aminoanthraquinone in high yield (Eq. (11)). The effective amines for this reaction might be somewhat different from those in the case of $PhNO_2$ (Table 22). However, the catalytic activities by rhodium catalysts seemed lower than those by ruthenium catalysts. A considerable attention should be paid to this exclusive catalytic

Table 21
Product distributions for the reduction of various aromatic nitro compounds using $Ru_3(CO)_{12}$-amine catalysts under CO/H_2O conditions [112]

Catalyst (mmol)	Reactant (mmol)	Product (mmol)	Products (gas phase/mmol)
$Ru_3(CO)_{12}$ /NEt_3 [a] (0.005/1.5)	1-nitroanthraquinone (10.2)	1-aminoanthraquinone (> 98%)	H_2(0.02): CO_2 (30.2)
$Ru_3(CO)_{12}$ /$HN(i\text{-}Pr)_2$ [b] (0.01/1.5)	*o*-chloronitrobenzene (5.0)	*o*-chloroaniline (> 99%)	H_2(< 0.4): CO_2 (14.7)
$Ru_3(CO)_{12}$ /pyrrolidine [a] (0.01/0.045)	1-nitroanthraquinone (10.2)	1-aminoanthraquinone (> 98%)	H_2(0.08): CO_2 (34.2)
$Ru_3(CO)_{12}$ /$HN(i\text{-}Pr)_2$ [b] (0.01/1.5)	benzonitrile (5.0)	no reaction	H_2(< 0.4) and CO

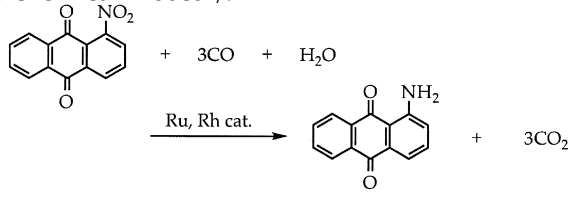
Reaction conditions: CO 20 atm, 150°C.
[a] MeOH/H_2O = 15/5 ml, 5 h.
[b] Diglyme/H_2O = 15/5 ml, 2 h.

Table 22
$Rh_6(CO)_{16}$ – Amine catalyzed reduction of 1-nitroanthraquinone yielding 1-aminoanthraquinone under CO/H_2O conditions

Amine	Molar ratio [a]	Solvent	Turnovers after 2 h [b]
None	—	diglyme	1158
Imidazole	1	diglyme	1356
9,10-Diamino-phenanthrene	10	diglyme	1422
NEt_3	50	diglyme	1506
$N(n\text{-}Pr)_3$	10	diglyme	1500
$HN(i\text{-}Pr)_2$	50	diglyme	1824

Reaction conditions: $Rh_6(CO)_{16}$ 0.005 mmol, solvent/H_2O = 15/5 ml, 1-nitroanthraquinone 10.2 mmol, CO 20 atm, 150°C, 2 h.

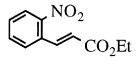
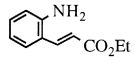
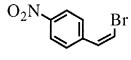
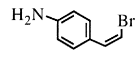
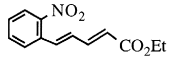
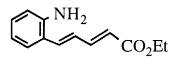
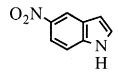
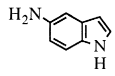
process especially from industrial viewpoints, because 1-aminoanthraquinone is one of the key intermediates as dye in the chemical industry.



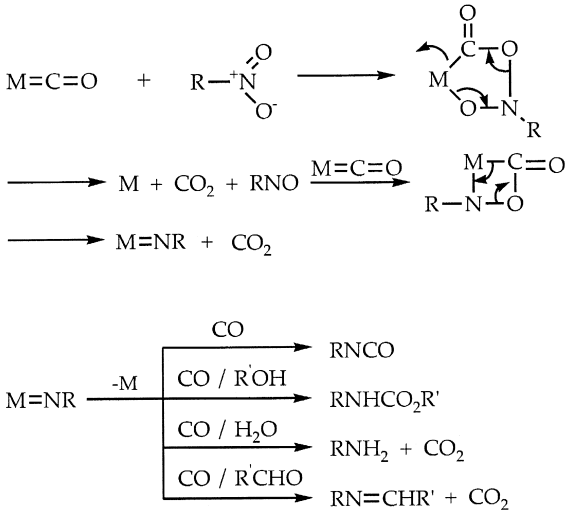
(11)

Kaneda et al. recently showed that the reduction of aromatic nitro groups with CO and water catalyzed by the previously reported $Rh_6(CO)_{16}$–$Me_2N(CH_2)_3NMe_2$ system proceeded with high

Table 23
Chemoselective reduction of aromatic nitro compounds by $Rh_6(CO)_{16}$ – TMPDA catalyst under CO/H_2O conditions [114]

$ArNO_2$	$ArNH_2$	Yield / %
		95
		80
		90
		97
		74
		85
		95

Reaction conditions: $Rh_6(CO)_{16}$ 0.0125 mmol, TMPDA 2.5 mmol, 2-ethoxyethanol/H_2O = 4/0.72 ml, CO 2–8 atm, 5 h, substrates 1.25 mmol.
TMPDA = N,N,N',N'-tetramethyl-1,3-propanediamine.



Scheme 5.

selectivity toward aromatic nitro-groups to afford the corresponding aromatic amines in good yield (Table 23) [114]. The polymer supported catalyst showed the similar properties.

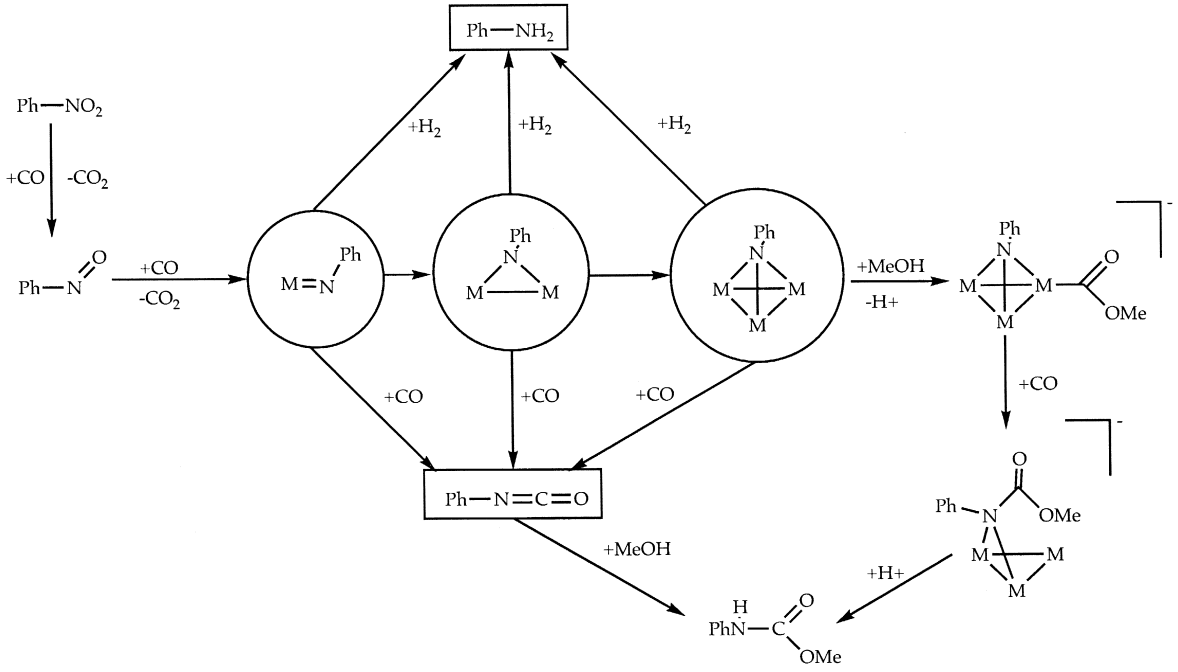
More recently, Tafesh and Beller at Hoechst employed palladium complexes involving water-soluble ligands such as TPPTS or BINAS (a mixture of tetra, penta and hexa-sulfonated 2,2′-bis diphenylphosphinomethylene binaphthyl) for reduction of various aromatic nitro compounds under CO (60–120 bar) and H_2O conditions [115]. Remarkable improvement of both catalytic activity and selectivity toward aromatic nitro compounds was, however, not observed in these catalytic reactions.

3.3. Considerations for the reaction pathway for the ruthenium catalyzed exclusive reduction of aromatic nitro-group with CO and H_2O

It has been postulated that the reaction of aromatic nitro compounds involves successive oxygen transfer reactions between the nitro compounds and coordinated metal–carbonyl ligand [116,117]. In addition, this can be explained in terms of cycloaddition of $ArNO_2$ and ArNO to a metal–carbonyl double bond followed by extrusion of carbon dioxide, as shown in Scheme 5.

It has also often been suggested for carbonylation or reduction of nitrobenzene by ruthenium catalyst that metal imido ligands bound to one, two or three metal atoms that was generated by the stepwise deoxygenation of nitrobenzene, nitrosobenzene would be hydrogenated to give aniline, whereas carbonylation gave phenyl isocyanate, as shown in Scheme 6 [118–120] [1]. Therefore, the reduction of nitrobenzene was believed to be effected by the hydrogenation of metal–nitrene species, because the ruthenium-cluster nitrene complex was hydrogenated to afford aniline as shown below (Eq. (12)) [120], and the reduction using ruthenium–carbonyl complexes in the presence of NMe_3 accompanied formation of an excess amount of hydrogen gas that was generated from the water–gas shift reaction [83,84,107].

[1] In this paper, aniline was obtained by hydrogenation of metal–nitrene complex, and therefore, proposed that the reduction of nitrobenzene under CO/H_2O by $Ru_3(CO)_{12}$ proceeds by a hydrogenation of metal–nitrene.



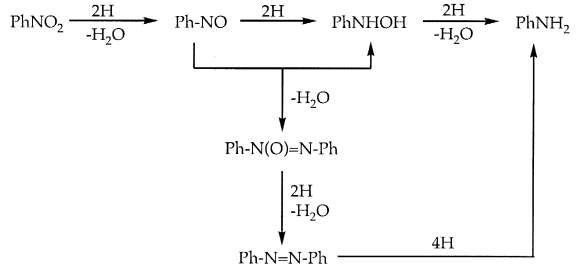
Scheme 6.

$$Ru_3(CO)_{12} + PhNO_2 \xrightarrow[-2CO_2]{} Ru_3(CO)_{10}(NPh)$$

$$Ru_3(CO)_{10}(NPh) \xrightarrow[-CO]{H_2} Ru_3H_2(CO)_9(NPh) \qquad (12)$$

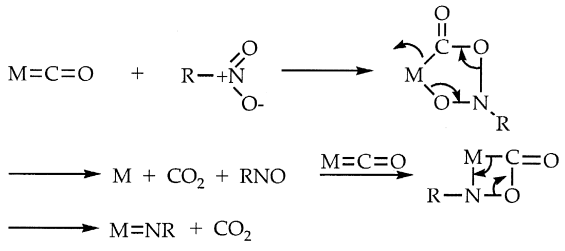
$$Ru_3H_2(CO)_9(NPh) \xrightarrow{3CO} Ru_3(CO)_{12} + PhNH_2$$

Alessio et al. also presented another possibility, that the reduction of nitrobenzene using $Ru_3(CO)_{12}$ with 3,4,7,8-tetramethyl-1,10-phenanthroline proceeded by a simple hydrogenation of aromatic nitro compounds catalyzed by palladium-, and platinum–carbon catalysts (Scheme 7) [91–94]. Shvo et al.

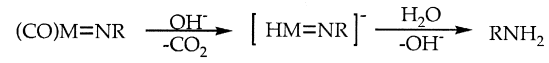


Scheme 7.

1) Formation of Metal-Nitrene Species

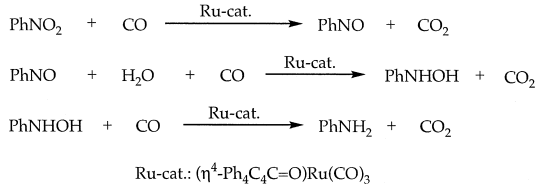


2) Intramolecular hydrogen transfer reaction



Scheme 8.

proposed a multi-step catalytic reduction scheme for the reduction using (η_4-$Ph_4C_4C{=}O)(CO)_3Ru$ via PhNHOH as shown below (Eq. (13)) [108].



(13)

As mentioned above, the reduction of aromatic nitro groups using ruthenium–carbonyl complexes in the presence of NEt_3, and $HN(i\text{-}Pr)_2$ proceeded with exclusive selectivity of aromatic nitro-groups [110–112], without accompanying hydrogen gas formation. Therefore, we believe, the reaction did not take place by hydrogenation from the WGSR. We proposed two possible reaction pathways for the exclusive reduction of aromatic nitro groups by ruthenium–carbonyl complexes in the presence of NEt_3, and $HN(i\text{-}Pr)_2$: (i) decarboxylation of isocyanates with water, or (ii) intramolecular hydrogen transfer between metal–nitrene and hydride, as shown in Scheme 8. We believe, the present catalytic reduction probably takes place by the exclusive intramolecular hydrogen transfer reaction [112].

4. Conclusion

The author has summarized recent results for hydrogenation of olefins and aldehydes by homogeneous catalysts in aqueous media. Recent reports for the reduction of aromatic nitro compounds by homogeneous transition metal catalysts under CO/H_2O conditions have also been summarized in this paper. As mentioned above, the potential importance of remarkable chemoselectivity on the hydrogenation of aldehydes, especially α,β-unsaturated aldehydes should be emphasized. The exclusive reduction of aromatic nitro groups by ruthenium catalysts under CO and water should also be emphasized from both synthetic and industrial viewpoints. Since the process in these catalysts should be more simplified compared to the conventional methods (ex. selectivity, after-treatment of by-prod-

ucts in stoichiometric reaction) as described above, the author expects, these catalytic processes will be replaced in the near future.

Acknowledgements

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