

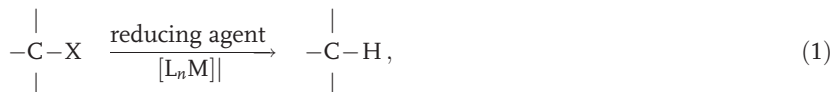
18 Dehalogenation Reactions

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18.1 Introduction

Reductive dehalogenation – one of the earliest reactions described in the organic chemical literature – has achieved special significance since the 1980s when the harmful properties of numerous halogenated (chiefly chlorinated) hydrocarbons became clear. The identification of methods capable of neutralizing or, at least, diminishing these dangers, remains a major challenge for chemistry. It is reasonable to convert stocks of the prohibited chemicals (e.g., polychlorobiphenyls, PCBs; chlorofluorocarbons, CFCs) to valuable products as far as possible. At the same time, the halogen-containing wastes should be detoxified by degradation. During the past two decades, the mainly heterogeneous (but also homogeneous) catalytic dehalogenation provided a major share towards solving these problems. Within this period, substantial progress was also made in the application of these reactions in organic syntheses.

Hydrodehalogenation – that is, hydrogenolysis of the carbon–halogen bond – involves the displacement of a halogen bound to carbon by a hydrogen atom. This chapter is devoted to dehalogenations mediated by transition-metal complexes (Eq. (1)):



where X = F, Cl, Br, I, and [L_nM] = a transition metal complex. The use of a wide variety of reducing agents (H₂, hydrides of metals and metalloids, organic reductants, etc.) under the most diverse reaction conditions (e.g., one- or two-phase systems) has been reported. Organic halides have also been reduced by electrochemical and photochemical methods in the presence of compounds of the type [L_nM]. Reductive transformations of organic halides not relevant to Eq. (1) (e.g., coupling reactions) and dehalogenation of acyl halides will not be included here.

The reactivity of the carbon–halogen bond in Eq. (1) depends on several factors:

- the nature of the halogen atom;
- the environment of the halogen atom in the molecule; and
- the reagents and conditions used in Eq. (1) [1].

The order of reactivity of the C–X bond (generally: I > Br > Cl > F) is consistent with its strength. For instance, the experimentally found dissociation energies for phenyl halides ($D_{\text{Ph-X}}$) are 528, 402, 339, and 272 kJ mol⁻¹ at 298 K for X = F, Cl, Br, and I, respectively [2]. Consequently, catalytic defluorination in the literature is comparatively rare. The different reactivity of the C–X bonds renders possible the selective dehalogenation of compounds containing two dissimilar halides, leaving intact the stronger C–X bond.

Table 18.1 Catalytic hydrodechlorination of chlorobenzene. ^{a)}

Catalyst/Reductant(s)	Solvent	Temperature [K]	TON ^{b)}	TOF ^{c)} [h ⁻¹]	Reference
[py ₃ RhCl ₃]/NaBH ₄ /H ₂	DMF	298	9.9 ^{d)}	0.76 ^{d)}	11
[(1,5-hexadiene)RhCl ₂]/H ₂ /Et ₂ NH	<i>p</i> -Xylene/H ₂ O	323	> 64 ^{d)}	–	12
[(Cy ₃ P) ₂ Rh(H)Cl ₂]/H ₂ /PhCH ₂ NEt ₃ ⁺ Cl ⁻ /NaOH	Toluene	298	19.4 ^{d)}	0.81 ^{d)}	13
[Cp* [*] RhCl ₂]/H ₂ /NEt ₃	<i>i</i> -PrOH	348	≥ 16.6 ^{d, e)}	5.55 ^{d)}	16
[(COD)RuCl ₂]/2PCy ₃ /H ₂ /NaOH	2-BuOH	353	39.6 ^{d)}	39.6 ^{d)}	20
RhCl ₃ /Aliquat 336/H ₂	CH ₂ Cl ₂	353	≥ 48.8 ^{d, e)}	2.71 ^{d)}	21
[(PPh ₃) ₄ Ni]/MgH ₂	THF	298	13.3 ^{d)}	0.74 ^{d)}	33
NiCl ₂ /MgH ₂	THF	298	≥ 50 ^{d)}	2.5 ^{d)}	34
[Cp ₃ Ln]/NaH	THF	319	5.6 ^{d)}	0.12 ^{d)}	35
Ni(OAc) ₂ /[Cp ₂ TiCl ₂]/NaH	THF	339	≥ 16.7 ^{d)}	8.33 ^{d)}	37
[(PPh ₃) ₃ Ni]/NaBH ₄	DMF	343	5.40 ^{d)}	0.23 ^{d)}	43
[(PhCH ₂ CN)PdCl ₂]/NaAlH ₂ (OCH ₂ CH ₂ OMe) ₃	Benzene	343	43.3 ^{d)}	9.63 ^{d)}	53
Pd(OAc) ₂ /Polymethylhydrosiloxane/KF	THF/H ₂ O	298	19.0 ^{d)}	66.7 ^{d)}	77
PdCl ₂ /indoline	MeOH	413	6.79 ^{d)}	1.70 ^{d)}	92
Pd(OAc) ₂ /2dipp ^{f)} /MeOH/NaOH	MeOH	373	90 ^{d)}	4.5 ^{d)}	100
Pd(OAc) ₂ /2dipp ^{f)} /HCO ₂ Na	MeOH	373	≥ 100 ^{d)}	≈ 5 ^{d)}	100
[Pd(dba) ₂]/3L/ <i>i</i> -PrOH/K ₂ CO ₃ ^{g)}	<i>i</i> -PrOH	353	1019	46.3 ^{d)}	103
[Cp* [*] Rh(OAc) ₂]/H ₂ O/2-BuOH/KOH	2-BuOH	371	38.4 ^{d, i)}	2.26 ^{d)}	106
[(IPr)Pd(allyl)Cl] ^{h)} / <i>t</i> -BuONa	<i>i</i> -PrOH	333	≥ 380 ^{d, i)}	109 ^{d)}	108
Ni(0)/IMes HCl ^{f)} / <i>i</i> -PrONa	THF	338	3.2 ^{d)}	3.2 ^{d)}	109
[Cp ₂ TiCl ₂]/BuMgCl	THF	298	7.4 ^{d)}	0.15 ^{d)}	116

a) Benzene product unless otherwise stated.

b) Mol converted substrate/mol catalyst.

c) Mol converted substrate/(mol catalyst × h).

d) Calculated from the experimental data of the author(s).

e) Cyclohexane product.

f) See text.

g) L = Dicyclohexyl-[(2,4,6-triisopropyl)phenyl]phosphine; 4-chloro-*α*-methylstyrene substrate, methylstyrene product.

h) IPr: *N,N'*-bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene.

i) 4-Chlorotoluene substrate, toluene product.

Table 18.2 Hydrodechlorination of PCBs and related compounds.^{a)}

Catalysts/Reductant(s)	Substrate	Solvent	Temperature [K]	Dechlorination [%] ^{b)}	TOF ^{c)} [h ⁻¹]	Reference
[(Et ₃ P) ₂ NiCl ₂]/NaBH ₂ (OCH ₂ CH ₂ OMe) ₂	3,3',4,4'-tetrachlorobiphenyl	THF	341	>99 ^{d)}	–	31
[(Et ₃ P) ₂ NiCl ₂]/NaBH ₂ (OCH ₂ CH ₂ OMe) ₂	Arochlor 1232 ^{e)}	THF	341	75 ^{d,f)}	–	31
[Cp ₂ TiCl ₂]/NaBH ₄ /py	Octachlorodibenzofuran	Bis(2-methoxyethyl)ether	398	100 ^{g)}	1.4 × 10 ^{-2h)}	48
Ni(acac) ₂ /NaAlH ₂ (OCH ₂ CH ₂ OMe) ₂	Delor 103 ⁱ⁾	Toluene	383	>99 ^{l)}	19.7 ^{h)}	56
Co(acac) ₂ /NaAlH ₂ (OCH ₂ CH ₂ OMe) ₂	Delor 103 ⁱ⁾	Toluene	383	>99 ^{l)}	56.9 ^{h)}	56
[(dppf)PdCl ₂] ^{k)} /NaBH ₄	4,4'-dibromobiphenyl	THF/TMEDA ⁱ⁾	298	100 ^{l)}	22.8 ^{h)}	67
Pd(OAc) ₂ /2PPh ₃ / <i>i</i> -PrOH/NaOH	Kanechlor 600 ^{m)}	<i>i</i> -PrOH	355	50 ^{d,f)}	0.24 ^{h)}	94
[ZnPCl] ^{l,m)}	Arochlor 1232 ^{e)}	DDAB ^{o)} /dodecane/H ₂ O (microemulsion)	298	>99.8	–	167
[ZnPCl] ^{l,m)}	Arochlor 1260 ^{m)}	DDAB ^{o)} /dodecane/H ₂ O (microemulsion)	298	94 ^{f)}	–	167
CeCl ₃ /LiAlH ₄	4,4'-dichlorobiphenyl	DME	358	>99	0.22 ^{h)}	214
NiCl ₂ /NaBH ₂ (OCH ₂ CH ₂ OMe) ₂	Arochlor 1016 ^{p)}	THF	341	90 ^{f,r)}	3.3 × 10 ^{-2h)}	215

a) Biphenyl product unless otherwise stated.

b) Conversion of PCB in % (w/w) unless otherwise stated.

c) mol converted substrate/(mol catalyst × h).

d) Determined by analysis of the Cl-content of the product.

e) Refined compound of mono- to tetrachlorobiphenyls with a majority of mono-, di-, and trichlorobiphenyls.

f) The product is a mixture.

g) Dibenzofuran product.

h) Calculated from the experimental data of the author(s).

i) Refined compound of di- to pentachlorobiphenyls with a majority of trichlorobiphenyls.

j) Determined by GC analysis.

k) See text.

l) Debromination % (w/w).

m) Refined compound of penta- to enneachlorobiphenyls with a majority of hexachlorobiphenyls.

n) Electrolysis: 1.07 mA cm⁻² on lead cathode.

o) Didodecyldimethylammonium bromide.

p) Refined compound of mono- to pentachlorobiphenyls with a majority of trichlorobiphenyls.

r) mol.%.

Table 18.3 Hydrodechlorination of carbon tetrachloride.^{a)}

Catalyst/Reductant(s)	Solvent	Temperature [K]	TON ^{b)}	TOF ^{c)} [h ⁻¹]	Reference
[(PPh) ₃ RuCl ₂]/H ₂ /(CH ₂ OH) ₂	Xylene	298	81	–	24
[(PPh) ₃ RuCl ₂]/H ₂ /Et ₃ N	Xylene	298	69	–	24
[(PPh) ₃ RuCl ₂]/Et ₃ SiH	–	353	778 ^{d)}	156 ^{d)}	74
[(PN)PtMeCl]/HSiMe ₂ Ph	Benzene	333	≥ 50 ^{d)}	11.1 ^{d)}	82
[(PTA) ₃ Ru(H ₂ O) ₃](tosylate) ₂ ^{e)} /HCOONa	H ₂ O	353	478	–	111
[RuCl ₂ (TPPMS) ₂] ^{f)} /HCOONa	H ₂ O	353	≈ 480 ^{d, g)}	≈ 160 ^{d)}	111
[RuCl ₂ (TPPMS) ₂] ^{f)} /HCOONH ₄	H ₂ O	353	416 ^{d)}	139 ^{d)}	111
CoTMPyP-SG ^{g)}	Phosphate buffer (pH = 7.5)	298	–	37.3	121
CoPcTs ^{h)}	Phosphate buffer (pH = 7.5)	298	–	35.8	121
Vitamin B ₁₂ /Ti(III)-citrate	MeOH	298	> 48 ^{d, g)}	> 2.66 ^{d)}	130
Cobinamide-dicyanide/Ti(III)-citrate	MeOH	298	> 48 ^{d, g)}	> 2.66 ^{d)}	130
Fe-porphyrin/cysteine	Phosphate buffer (pH = 7.0)	298	≈ 0.8 ^{d, i)}	–	136
Na ₄ [W ₁₀ O ₃₂] ^{k)}	DMF/ <i>i</i> -PrOH ^{f)}	295	≈ 49 ^{d)}	–	173
[Bu ₄ N][W ₁₀ O ₃₂] ^{k, l)}	DMF	295	40 ^{d, g)}	5 ^{d)}	173

a) Chloroform product unless otherwise stated.

b) Mol converted substrate/mol catalyst.

c) Mol converted substrate/(mol catalyst × h).

d) Calculated from the experimental data of the author(s).

e) PTA: 1,3,5-triaza-7-phosphaadamantane.

f) See text.

g) Mixture of products.

h) 5,10,15,20-tetrakis(1-methyl-4-pyridino)porphinecobalt(II) tetrachloride supported on silica gel.

i) Cobalt(II) phthalocyanine-tetrasulfonic acid, tetrasodium salt.

j) Complete degradation.

k) Irradiation with 1000-W high-pressure Hg lamp.

l) Under pure O₂.

The diversity of the substrates, catalysts, and reducing methods made it difficult to organize the material of this chapter. Thus, we have chosen an arrangement related to that used by Kesz and Saillant [3] in their review on transition-metal hydrides – that is, we have classified the subject according to the applied reducing agents. Additional sections were devoted to the newer biomimetic and electrochemical reductions. Special attention was paid mainly to those methods which are of preparative value. Stoichiometric hydrogenations and model reactions will be discussed only in connection with the mechanisms.

In order to facilitate the comparison of the effectiveness of the very diverse methods, turnover numbers (TON), and/or turnover frequencies (TOF) (if they were given by the author or could be calculated based on their data) are sum-

marized in the tables. The limited space available for this chapter allowed results to be compiled only for the dehalogenation of chlorobenzene (Table 18.1), for polychlorinated biphenyls and related compounds (Table 18.2), and for carbon tetrachloride (Table 18.3). To emphasize the environmental concerns, two of the three chosen compounds are common pollutants.

Despite catalytic hydrodehalogenation having been reviewed on several occasions, even when such reports contained data for homogeneous catalysis it was the information for heterogeneous which generally dominated [1, 2, 4–6]. The only comprehensive volume discussing only homogeneous hydrogenolysis, the classical handbook of James [7], was published more than 30 years ago.

18.2

Catalytic Dehalogenation with Various Reducing Agents

18.2.1

Molecular Hydrogen

This type of hydrodehalogenation has been performed generally in the presence of organic or inorganic bases to neutralize the hydrogen halides formed. Among published results, the use of rhodium complexes as catalysts dominates, but palladium and ruthenium complexes have also been applied on a frequent basis.

Although relatively few investigations have been published on the use of homogeneous hydrogenolysis of organic halides with molecular hydrogen, the first examples are rather old. During the 1960s, Kwiatek and coworkers [8] reduced a number of halogenated alkanes, alkenes, and alkynes with alkaline solutions of pentacyanocobaltate(II) under atmospheric hydrogen at 25 °C. The catalytic results, as well as their mechanistic interpretation, have been exhaustively reviewed [8, 9].

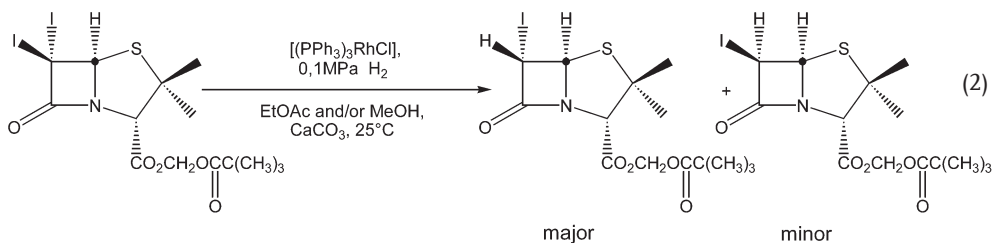
Roček and coworkers [10] attempted to compare the activity of various transition-metal complexes in the hydrodehalogenation of 5-iodouracil with atmospheric H₂ at 70–80 °C. The majority of the examined complexes decomposed to metal, but [(PPh₃)₂CoCl₂], and [(PPh₃)₃RuCl₂] in DMA (*N,N*-dimethyl-acetamide) remained homogeneous. The more active Ru complex catalyzed also the preparation of [5-2H]uracil using D₂ instead of H₂.

Love and McQuillin [11] have shown that the catalyst system [py₃RhCl₃]/NaBH₄ (1 : 1) in DMF (py = pyridine, DMF = *N,N*-dimethylformamide) is active in halogen/hydrogen exchange concerning several alkyl and aryl halides with atmospheric H₂. Interestingly, the reactivity orders ClC₆H₅ > BrC₆H₅, and PhCH₂Cl > PhCH₂Br have been found. (–)-2-Chloro-2-phenylpropanoic acid and its methyl ester were dechlorinated to produce almost totally racemic products.

Markó and coworkers [12] dehalogenated several alkyl and benzyl halides as well as halobenzenes (X = Cl, Br, I) with [(1,5-hexadiene)RhCl₂]/PPh₃ in the presence of Et₂NH using a medium of *p*-xylene/water at 50 °C and atmospheric H₂ pressure. Grushin and Alper [13] elaborated a similar (but more effective)

method for the hydrogenolysis of chloroarenes using [L₂Rh(H)Cl₂] (**1**) (L = PCy₃, Pi-Pr₃) as catalysts in a toluene/40% NaOH solvent system with benzyltriethylammonium chloride as a phase-transfer agent. The reaction occurred under mild conditions (25–100 °C, 0.1 MPa), and many functional groups (e.g., R, OR, CF₃, COAr, COOH, NH₂) were compatible with the C–Cl bond cleavage. Some chloro-substituted heterocycles were also readily dehalogenated. Hydrogenolysis of the C–F bond of 1-fluoronaphthalene with a similar catalytic system (**1**, L = PCy₃) could be performed at 95 °C and 0.5 MPa [14]. The use of the two-phase system improved the chance for the recovery of the catalysts [13, 14].

Setti and Mascaretti [15] realized the highly chemoselective and stereocontrolled hydrodehalogenation of the carbon-6-halogen bond of (pivaloyloxy)-methyl-6,6-dihalopenicillanate by [(PPh₃)₃RhCl] in EtOAc and/or MeOH solvent systems with atmospheric H₂. For the diiodo derivative (Eq. (2)):

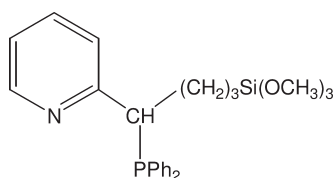


Ferrughelli and Horváth [16] converted chloroarenes into the corresponding saturated hydrocarbons by a system generated from [Cp₂RhCl₂] (Cp = η⁵-cyclopentadienyl) in the presence of Et₃N and 2-propanol under 4.1 MPa H₂ at 75 °C. For example, 1 mmol 1,2,4-trichlorobenzene was successively reduced to cyclohexane within 6 h using 0.03 mmol of catalyst. Aizenberg and Milstein [17] have reported on the effective and selective hydrogenolysis of some polyfluorinated arenes. Heating [L₃RhY] (L = PMe₃, Y = C₆F₅ or H) at 95–100 °C in C₆F₆ or C₆F₅H in the presence of a base under 0.6 MPa of H₂ led to the displacement of one of the F atoms by H with selectivities >92%. Jones' group realized a quasicatalytic hydrogenolysis of hexafluorobenzene: heating the solution of [Cp*⁺Rh(H)₂PMe₃] (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) and C₆F₆ at 135 °C for 25 days under 0.1 MPa of H₂, they produced 1.4 equiv. of C₆F₅H based on the starting rhodium complex [18].

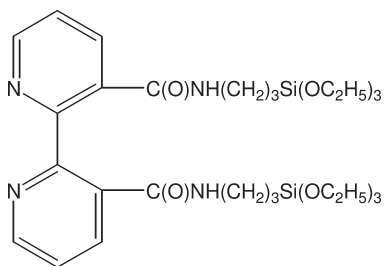
Angeloff, Brunet and colleagues [19] have found [(PPh₃)₄Pd] to be an efficient catalyst for the selective conversion of 2,3-dichloronitrobenzene into 3-chloronitrobenzene at 120 °C under atmospheric H₂. The reaction could be stopped at the maximum selectivity (>90%). Nolan, Grubbs, and associates [20] have described that [(PCy₃)₂Ru(H)₂(H₂)₂] and *in-situ*-generated [L₂Ru(H)Cl(H₂)₂] (from [(COD)-RuCl₂]_x (COD = 1,5-cyclooctadiene) and 2L, L = PCy₃ or Pi-Pr₃) hydrogenolyze aryl chlorides completely in alcohols as solvents at 80 °C under 0.3 MPa of H₂ within 1 h. [(PCy₃)₂Ru(H)Cl(H₂)₂] was very active also in the transfer hydrogenolysis of

chloroarenes in *sec*-butyl alcohol. The systems exhibited significant functional group tolerance.

The heterogenization as a method for recycling of organotransition metal catalysts has also been studied in the case of haloarene hydrogenolysis. Blum's group [21] reported that the SiO₂ sol-gel entrapped ion pair [(C₈H₁₇)₃NMe]⁺[RhCl₄·nH₂O]⁻, generated from RCl₃·3H₂O, Aliquat 336, and Si(OMe)₄ catalyzes the hydrogenation of aryl fluorides and chlorides to give cyclohexane derivatives at 80 °C and 1.6 MPa of H₂. Fluorobenzenes, however, were proved to lose HF in a noncatalytic process. The catalyst was leach-proof and recyclable, with little or no loss in activity. Angelici and coworkers [22] have developed a process using the complexes [(COD)Rh(2)]BF₄ and [(COD)Rh(3)]BF₄ tethered on a heterogeneous catalyst, Pd/SiO₂. Fluorobenzene and 1,2-difluorobenzene were reduced under very mild conditions (0.4 MPa H₂, 70 °C) in the presence of NaOAc. The supported catalyst was more active than Pd/SiO₂ or the starting rhodium complexes alone.



(2)



(3)

It has not been shown unambiguously, however, whether the rhodium remains coordinated to the ligands **2** and **3** during the catalysis. Kantam and associates [23] have used a Pd(II) catalyst anchored onto MCM-41/silylamine (MCM-41: a molecular-sieve) for hydrodehalogenation of aryl halides by atmospheric hydrogen. The catalyst was reused for several cycles with constant activity.

During the past ten years, several research groups have attempted to catalyze homogeneously the dechlorination of chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) compounds. Roundhill and associates [24] have studied the transformation of CCl₄ to CHCl₃, and that of CFCl₃ to CHFCl₂ in the presence of [(PPh₃)₃RuCl₂] and [(dppe)₂RuCl₂] (dppe = 1,2-bis(diphenylphosphino)ethane) at 25 °C and 0.11 MPa. The first transformation occurred more easily

than the second (TONs up to 90 could be reached in 5–14 days in the former case; see Table 18.3). Lee and colleagues [25, 26] achieved efficient and selective hydrodechlorination of CF_3CCl_3 to CF_3CHCl_2 , as well as $\text{CF}_2\text{ClCFCl}_2$ to $\text{CF}_2\text{ClCHClF}$ and $\text{CFCl}=\text{CCl}_2$, by the use of Group VIII transition metal complexes at 80–150 °C and about 1 MPa H_2 pressure. In the case of the most effective catalyst, $[\text{RhCl}(\text{PPh}_3)_3]$, a slightly polar solvent such as tetrahydrofuran (THF) was found to be appropriate for selective hydrogenolysis of CFCs. Mingos and Vilar [27, 28] synthesized the novel methylidyne cluster compounds $[(\text{Pt-Bu}_3)_4\text{Pd}_4(\mu_3\text{-CY})(\mu\text{-Cl})_3]$ (**4**) from $[\text{Pd}_2(\text{dba})_3]$ (dba = dibenzylideneacetone) and Pt-Bu_3 in the presence of the halides CYCl_3 (Y = H, F). In toluene/ Et_3N , **4** catalyzed the transformation of CFCl_3 into CH_3F and CHFCl_2 with atmospheric H_2 . Under similar conditions with $[(\text{Pt-Bu}_3)_2\text{Pd}]$, CFCl_2H was the only hydrogenation product. Recently, Sisak and coworkers [29] have found that $[\text{py}_3\text{RhCl}_3]$ – in the presence of pyridine as a base – and *in-situ*-generated $[(\text{Pi-Pr}_3)_3\text{Pd}]$, surpassed $\text{Pd}/\text{Al}_2\text{O}_3$, the most active heterogeneous catalyst tested in the selective conversion of CF_3CHFCl into $\text{CF}_3\text{CH}_2\text{F}$ at 120 °C and 8–10 MPa H_2 pressure. The dechlorination of CHFCl_2 and CF_2Cl_2 with the same catalysts, however, could be performed only at higher temperatures, and hydrodefluorination of the substrates also occurred.

18.2.2

Simple and Complex Metal Hydrides

Simple and complex metal hydrides are capable of reducing organic halides due to their nucleophilic character. The efficiency of these reducing agents can be increased considerably by adding stoichiometric or catalytic amounts of various transition-metal compounds. Initially, hydrides and simple metal salts (without any stabilizing ligands) were combined, and although these catalytic systems were qualified only rarely as definitely *heterogeneous* (for example, see [30]), it is questionable whether they are in fact *homogeneous*, or not (see [31, 32]). Similar problems arose in the case of the application of simple metal salts together with other reducing agents (*vide infra*).

Carfagna and coworkers [33] found that Ni(0) and Pd(0) tertiary phosphine complexes activate MgH_2 and MgD_2 in the reduction of organic halides. The more active $[(\text{PPh}_3)_4\text{Ni}]$ promoted the reduction of chlorobenzene, whereas $[(\text{PPh}_3)_4\text{Pd}]$ promoted only that of bromo- and iodobenzene to benzene (deuterobenzene) at room temperature or at 67 °C, respectively, in THF. The same authors [34] also tested several transition-metal salts as promoters in the hydrodehalogenation of halobenzenes with MgH_2 . NiCl_2 proved to be the most active, hydrogenolyzing even the C–F bond at 67 °C. A $[\text{Cp}_3\text{Ln}]/\text{NaH}/\text{THF}$ system has been reported to dehalogenate aryl halides with moderate activity at 45–65 °C [35]. Bromochlorobenzenes gave chlorobenzene selectively. The dimeric organolanthanide hydrides, $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{LaH}]_2$ hydrogenolyzed *p*-bromoanisole and 1-bromohexadecane catalytically under similar conditions [36].

Aromatic halides such as chlorobenzene and *p*-fluorotoluene were rapidly hydrogenolyzed in 100% conversion by NaH of nanometric size in the presence of homogeneous catalysts. One- or two-component (e.g., Ni(OAc)₂/TiCl₄) systems were effective. The combination of ytterbium chloride and a transition-metal chloride showed a remarkable synergistic effect [37, 38].

Dzhemilev and associates [39–41] prepared monohalocyclopropanes and cyclopropanes by the reductive dehalogenation of alkyl- and aryl-substituted *gem*-dihalocyclopropanes with *i*-Bu₂AlH in the presence of catalytic amounts of titanium and zirconium complexes. The stereochemistry of the reductions has been also studied. Very recently, Knight and coworkers [42] hydrogenolyzed racemic bromoalkanes using *i*-Bu₂AlH or *i*-PrMgCl in stoichiometric, and chiral, single-enantiomer titanium complexes in catalytic amounts at 0 to 110 °C. There was no detectable difference in the reduction rate between the two enantiomers of the alkyl halide. An enantiomerically pure secondary bromide was reduced under the same conditions without racemization during the course of the reaction.

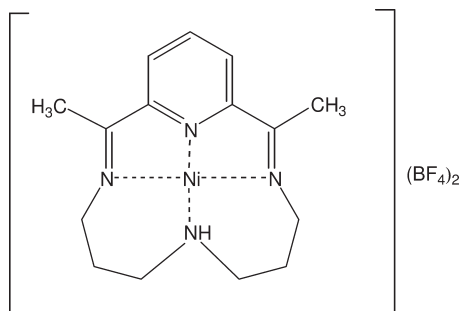
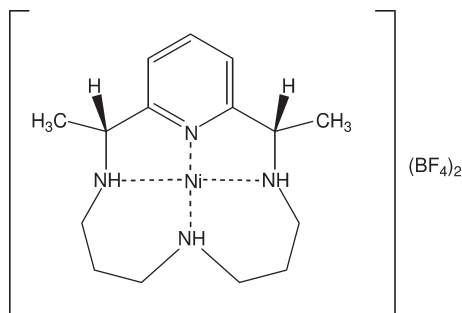
As early as 1979, Roth's group [43] reported that aryl bromides could be reduced with a homogeneous system generated from [(PPh₃)₂NiCl₂] and NaBH₄ in DMF at 70 °C. The same group [44] later studied the reduction of a series of pure PCB congeners with NaBH₄. Extensive hydrogenolysis occurred in the presence of a Ni(0) triphenylphosphine complex at ambient temperatures in DMF. High selectivity for 2-, 3-, and 4-chloro displacement from di- and trichlorobiphenyls has been found. The solvent properties determined the catalytic efficiency in the transformation of 1,2,3-trichlorobenzene with a related system at 70 °C: using ethanol/pyridine solvent mixtures, benzene was produced a high rate [45].

The [Cp₂TiCl₂]/NaBH₄ system has been studied by several groups. Meunier [46] observed that the dehalogenation of iodobenzenes in DMF at 70 °C requires the presence of molecular oxygen. In a later and more exhaustive study, Schwartz and coworkers [47, 48] found the reaction scope and mechanism of the haloarene reduction by this system to be solvent-dependent. At 85–93 °C in DMF, halogen/hydrogen exchange and the formation of dimethylamino-substituted byproducts were observed. In DMA or in ethers, however, only dechlorinated products resulted. The [Cp₂TiCl₂]/NaBH₄/amine systems reduced catalytically pollutants such as PCBs and DDT (1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane) [49]. Kim and coworkers [50, 51] reported that [Cp'₂MCl₂] (Cp' = Cp or Cp*; M = Ti, Zr, Hf) in the presence of several metal hydrides or alkyls catalyzes the conversion of monohalopyridines to give pyridine at room temperature. The effectiveness decreased as follows: Ti > Zr > Hf. The order of the aryl halide reactivity was surprising: C–F > C–Cl > C–Br. The reaction rate was boosted by adding 4 Å molecular sieves. Very recently, monofluoroaromatics have been reduced to the corresponding aromatic hydrocarbons when treated with the NbCl₅/LiAlH₄ system [52].

Several Czech research groups have studied the dehalogenation with NaAlH₂(OCH₂CH₂OCH₃)₂ (5). Hydrogenolysis of haloarenes with this hydride was accelerated by transition-metal species formed *in situ* from [(RCN)₂PdCl₂] (R = Ph, PhCH₂) [53] or from 2,4-pentanedionates [54–56]. In the latter case, the efficiency decreased in the order Co ≈ Ni ≈ Pd > Cu ≫ Mn > Fe [54]. Complete

conversion of the PCB liquid Delor 103 (42.6% Cl) to biphenyl has been effected in toluene with 5 and catalytic amounts of Ni(II) and Co(II) 2,4-pentanedionates at elevated temperatures [56].

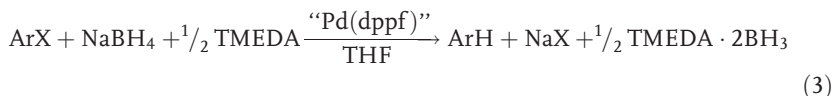
Sharf's group [57–59] has investigated Rh and Ru complexes with various ligands immobilized on the surface of silica gels modified with, for example, γ -aminopropyl groups (γ -AMPS), or polymers containing 3(5)-methyl-pyrazole and imidazole groups. $[\text{Rh}_2(\text{OAc})_4]$ immobilized on γ -AMPS dehalogenated *p*-bromotoluene by transfer of hydrogen from NaBH_4 and 2-propanol [57]. The immobilized binuclear Ru(II)-Ru(III) tetraacetate exhibited higher catalytic activity in the hydrogenolysis of *p*-bromotoluene than the heterogenized mononuclear systems [58]. The same authors [59] hydrogenolyzed *gem*-dihalocyclopropanes partially in the presence of the system Rh(I)- γ -AMPS/ NaBH_4 /CaO/2-propanol.



The Ni(II) complexes 6 and 7 have been found by Stiles [60] to be soluble catalysts for reductive dehalogenation when combined with NaBH_4 or hydrazine at 25–45°C in protic solvents. Reactivity toward the reducing system increased with the halogen content of the substrate. Aryl bromides were converted much faster than chlorides, polychlorobenzenes, however, reacted readily with stepwise loss of chlorine.

The dehalogenation of several types of polyhalogenated arenes has been studied by Hor's group [61–67]. Brominated thiophenes and bithiophenes were re-

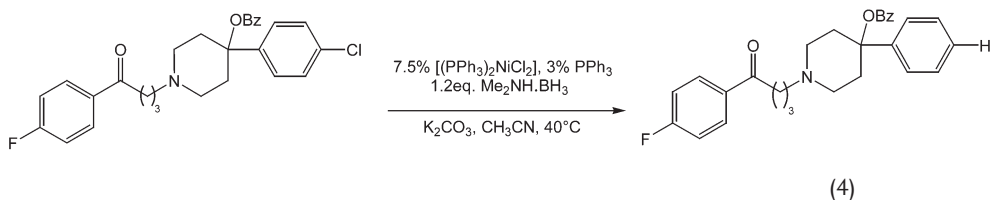
duced regioselectively using NaBH_4 in the presence of numerous Ni and Pd complexes as catalysts (e.g., 2,3,5-tribromothiophene afforded isomerically pure 2,3- or 2,4-dibromothiophene depending on the catalyst). The extent of debromination was controlled by the stoichiometry and substrate quantity. Pd-containing catalysts produced greater regioselectivity [61–63]. A variety of catalysts hydrogenolyzed 4,4'-dibromobiphenyl [64] as well as polybromobenzenes [65, 66] at room temperature, and complete conversions to biphenyl and benzene, respectively, has been achieved. The most satisfactory catalysts were generated *in situ* from the complexes $[(\text{dppf})\text{PdCl}_2]$ or $[(\text{dppf})_2\text{Pd}]$ ($\text{dppf} = 1,1'$ -bis(diphenylphosphino)ferrocene), NaBH_4 as a hydrogen source, and TMEDA (N,N,N',N' -tetramethylethylenediamine) as a supporting base and THF as a solvent (the addition sequence of the reactants was critical) [64, 65] (Eq. (3)):



A convenient one-pot system was developed also for the conversion of highly chlorinated benzenes to less chlorinated ones at room temperature, with reasonable conversion rates using the system $[(\text{dppf})\text{PdCl}_2]/\text{NaBH}_4/\text{TMEDA}/\text{THF}$ [67]. Degradation to benzene could not be achieved. Removal of chlorines in *meta*-position was preferred over those in *ortho*- or *para*-positions. The effectiveness of the method has been tested on the PCB mixtures Aroclor 1242, 1248, and 1254 at 67 °C.

King and coworkers [31] have used homogeneous organophosphorus–nickel complexes to detoxify PCBs by catalyzed hydrodechlorination using $\text{NaBH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ in boiling THF. In model experiments with decachlorobiphenyl, the cone angle of the organophosphorus ligand was shown to be a key factor controlling the magnitude and position of chlorine displacement. Significantly, the highly toxic, coplanar dioxin precursor 3,3',4,4'-tetrachlorobiphenyl, a *meta-para* chlorine-substituted congener, was dechlorinated quantitatively with a PEt_3 -containing catalyst system.

Organic analogues of metal hydrides have been applied recently as reductants in homogeneous hydrodehalogenations. Treatment of aryl halides containing other functional groups with catalytic amounts of $[(\text{PPh}_3)_2\text{NiCl}_2]/\text{PPh}_3$ in the presence of 1 equiv. $\text{Me}_2\text{NH} \cdot \text{BH}_3$ and a base under mild conditions resulted in halogen/hydrogen exchange products. Noteworthy was the clean dehalogenation of densely functionalized haloperidol benzoate (Eq. (4)), attesting to the functional group compatibility offered by this combination of reagents [68].



The novel, low-melting-point salt [N-pentylpyridinium][*closo*-CB₁₁H₁₂] has been used as solvent in several dehalogenations of mono- and polychlorides and -bromides, catalyzed by several Pd phosphine complexes [69]. The debromination of hexabromo- and 1,2,4,5-tetrabromobenzene was accomplished quite rapidly, whereas the dechlorination of 1,2,4-trichlorobenzene proceeded more slowly, but with excellent selectivity to 1,2-dichlorobenzene. The system could be recycled at least seven times without noticeable decrease of activity.

18.2.3

Hydrosilanes and Hydrostannanes

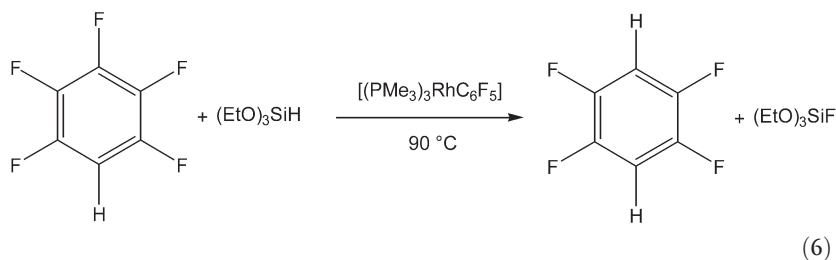
Hydrosilanes have a low ability to donate hydride or a hydrogen atom (cf. Section 18.2.2), but they are also useful reducing agents in combination with transition-metal complexes (Eq. (5)) [70]:



The problem of *homogeneity-heterogeneity* mentioned in Section 18.2.2 arises also here in the cases of using a simple metal salt instead of a ligand-stabilized salt (see [70, 71]).

Freidlina and coworkers [72, 73] were the first to use hydrosilanes for reducing organochlorine derivatives catalyzed by transition-metal complexes. For example, 1,1,1,5-tetrachloropentane was transformed into 1,1,5-trichloropentane by [Fe₂(CO)₉], and 1,3,3,5-tetrachlorodecane into 1,3,5-trichlorodecane by [Mn₂(CO)₁₀], respectively. Kono's group [74] has described the dechlorination of polychloroalkanes by silicon hydrides and in the presence of Ru(II) phosphine complexes as catalysts. CCl₄, CH₃CCl₃ and 1,1,1,3-tetrachloroalkanes have been reduced selectively to give CHCl₃, CH₃CHCl₂ and 1,1,3-trichloroalkanes with high turnovers at 80–100 °C (see Table 18.3). Pri-Bar and Buchman [75] hydrodehalogenated aryl iodides and bromides by polymethylhydrosiloxane (PHMS) using [(PPh₃)₄Pd] as a catalyst and Bz₃N as a base in Me₂SO/MeCN solvent mixtures at 60–110 °C. The debromination took place with a notable functional group tolerance. Recently, Maleczka and coworkers [76] developed a similar, but more powerful, method by fluoride activation of PMHS. In this case, the hydrodehalogenations of bromo- and iodoarenes were carried out in an amine-free system using THF as a solvent with relatively low loads of [(PPh₃)₂PdCl₂] catalyst. The same authors [77] reduced chloroarenes using catalytic amounts of Pd(OAc)₂ in combination with PMHS and aqueous KF at room temperature. The mildness of these methods was demonstrated by its functional group tolerance.

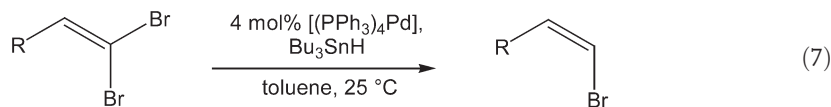
Aizenberg and Milstein [78] have found rhodium complex-catalyzed reactions between polyfluorobenzenes and hydrosilanes which resulted in the substitution of fluorine atoms by hydrogen and were both chemoselective and regioselective (Eq. (6)):



Esteruelas, Herrero and associates [79–81] have studied the simultaneous dechlorination of polychlorinated substrates and chlorination of Et_3SiH catalyzed by several complexes of Group VIII. The Os and Ir derivatives were less effective catalysts than those of Ru and Rh, and the former ones underwent deactivation during polychloroarene hydrogenolysis [79, 80]. Very recently, the same group showed that hexachlorocyclohexanes and Et_3SiH in the presence of various Rh and Ru complexes (e.g., $[(\text{PPh}_3)_3\text{RhCl}]$, $[(\text{P}i\text{-Pr}_3)_2\text{RhH}_2\text{Cl}]$, $[(\text{PPh}_3)_3\text{Ru}(\text{H})\text{Cl}]$, and $[(\text{P}i\text{-Pr}_3)_2\text{Ru}(\text{H})\text{Cl}(\text{H}_2)]$), afford cyclohexane/cyclohexene/benzene mixtures and Et_3SiCl . The reactivities of the substrates decreased in the order $\gamma > \alpha > \delta$ -hexachlorocyclohexane [81].

Schubert's group [82, 83] has discovered that the reactivity of Pt(II) complexes is enhanced towards organosilanes by employing hemilabile chelating ligands such as $\text{Me}_2\text{NCH}_2\text{CH}_2\text{PPh}_2$ ($\text{P}\cap\text{N}$). Thus, the complex $[(\text{P}\cap\text{N})\text{PtMeCl}]$ catalyzed the hydrogenolysis of R-Cl compounds by Me_2PhSiH to give R-H and Me_2PhSiCl at $60\text{ }^\circ\text{C}$ in benzene [82].

The dehalogenation of organic halides by organotin hydrides takes place in most cases with a free-radical mechanism [1, 84, 85]. The stereospecific reduction of 1,1-dibromo-1-alkenes with Bu_3SnH discovered by Uenishi and co-workers [86–89], however, did not occur in the absence of palladium complexes and did not involve radicals. For the synthesis of (*Z*)-1-bromo-1-alkenes, $[(\text{PPh}_3)_4\text{Pd}]$ proved to be the most effective catalyst which could also be generated *in situ*. The reaction in Eq. (7) proceeded at room temperature and a wide range of solvents could be used.



The authors determined the optimal reaction conditions and illustrated the scope of the method with 32 different starting compounds including alkenyl-, alkenyl-conjugated and 2,2-disubstituted 1,1-dibromo-1-alkenes.

18.2.4

Hydrogen Donors other than Hydrides

Various reagents have been found to be capable of donating hydrogen to transition metals in low valent state (e.g., formates, cyclic amines, alcohols in the presence of ligands and/or in basic medium). The reduction of transition-metal salts with metal alkyls (e.g., Grignard reagents with alkyl groups having β -hydrogen) may be regarded in close relation to their reactions with alcohol/base systems. The hydrogen transfer takes place from a metal-coordinated group both for alcoholates and for metal alkyls [3].

The dehalogenation of activated organic halides (e.g., benzyl halides and α -halo-ketones) was first published with various non-hydridic hydrogen donors. Grigg and coworkers [90] hydrogenolyzed activated organic halides with some noble metal chlorides (e.g., $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$) as catalysts in the presence of an alcohol and an excess of PPh_3 . A very intriguing reducing agent, *N*-benzyl-1,4-dihydropyridin-2(1H)-one (BNAH) as a NAD(P)H model has been applied by Yasui and associates [91]. Aryl iodides and activated alkyl halides were reduced with the system $[(\text{PPh}_3)_3\text{RhCl}]/\text{BNAH}$ in good yields at 70°C in MeCN. Secondary cyclic amines proved to be useful reducing agents for the transfer hydrogenolysis of aryl halides with PdCl_2 as a catalyst in methanol at 140°C . Indoline had the highest hydrogen-donating ability, and various bases (e.g., KOH) promoted the reaction [92].

Cortese and Heck [93] were first to report the application of palladium(0) triaryl phosphine complexes for homogeneous catalytic halogen/hydrogen exchange. The $\text{Pd}(\text{OAc})_2/\text{PAr}_3/\text{HCOOH}/\text{Et}_3\text{N}$ ($\text{Ar}=\text{Ph}$, *o*-tolyl, 2,5-*i*-Pr₂C₆H₃) systems reduced bromoarenes at 50°C , and the $\text{P}(\text{o-tolyl})_3$ -containing catalyst converted *m*-bromonitrobenzene selectively to nitrobenzene. Okamoto and Oka [94] dehalogenated aryl bromides by heating them with NaOH in alcoholic solvents in the presence of RhCl_3 or $\text{Pd}(\text{OAc})_2$ and PPh_3 . The method was suitable for destroying aromatic polyhalides. For example, $(\text{C}_6\text{Br}_5)_2\text{O}$ was transformed into $(\text{C}_6\text{H}_5)_2\text{O}$ in 2-propanol with more than 80 turnovers when treated for 5 h at 82°C . Helquist has applied sodium methoxide [95] and formate [96] as reducing agents for the hydrogenolysis of haloarenes with 5 mol.% of $[(\text{PPh}_3)_4\text{Pd}]$ in DMF at 100°C . In the case of formate, the debromination was really compatible with various functional groups.

Sasson and Rempel [97] showed that the system $[(\text{PPh}_3)_3\text{RuCl}_2]/\text{secondary alcohol}$ is suitable for the selective transformation of 1,1,1,3-tetrachloro into 1,1,3-trichloro compounds. Similarly, Blum and coworkers [98, 99] employed $[(\text{PPh}_3)_3\text{RuCl}_2]$ as well as polystyrene-anchored Rh, Ru and Ir complexes for the hydrogen transfer from alcohols to trihalomethyl compounds, leading to dihalomethyl derivatives. For example, one of the Cl atoms of 2,2,2-trichloro-1-phenylethanol was displaced by H at $140\text{--}160^\circ\text{C}$ in 2-propanol. The polymer-anchored catalysts proved to be resistant to leaching [99].

Milstein and colleagues [100] have developed very efficient methods using basic, chelating phosphine ligands. Even aryl chlorides underwent reductive dechlorination to the corresponding arenes with $[(\text{dipp})_2\text{Pd}]$ as catalyst (dipp,

dippe, dippb = 1,3-bis(diisopropylphosphino)propane, -ethane, -butane) with high yields. The systems exhibited high functional group tolerance. Base-sensitive groups (e.g., CHO, CN) did not survive the conditions of the NaOH/MeOH reducing system, but remained unaffected when treated with HCO₂Na in MeOH or DMF. Dipp homologues were also effective ligands (reactivity order: dipp > dippb > dippe). Beletskaya and associates [101] have reported that using the system [Pd(dba)₂]/dppf/NaOt-Bu/dioxane the formation of dialkyl anilines from *m*- and *p*-dibromobenzenes and secondary amines – that is, the exchange of one of the Br atoms to H became the main process. [(PPh₃)₂PdCl₂] or [(PPh₃)₄Pd] catalyzed the deiodination of 5-iodopyrrole-2-carboxylates with HCOONa to give the corresponding 5-unsubstituted pyrrole-2-carboxylates in good yields [102]. Very recently, the C–Cl bond of various chloroarenes was reduced by [Pd(dba)₂]/phosphine/K₂CO₃/*i*-PrOH systems at 80 °C with very remarkable turnovers (see Table 18.1) [103].

Dicyclohexyl-[(2,4,6-triisopropyl)phenyl]-phosphine proved to be the most suitable ligand for the functional group-friendly hydrogenolysis. Rapid and specific deuterium labeling has been achieved through the microwave-enhanced dehalogenation of a number of *N*-4-picolyl-4-halogenobenzamides using deuterated formate as solid deuterium donor and Pd(OAc)₂, RhCl₃ or [(PPh₃)₃RhCl] as catalysts in dimethyl sulfoxide (DMSO) [104]. Polychloroarenes could be dehalogenated with HCOONa in 2-propanol using [(PPh₃)₃RhCl] catalyst. For example, the hydrogenolysis of 1,2,4-trichlorobenzene proved selective for 1,2-dichlorobenzene [105]. Fujita and colleagues [106] have achieved effective transfer hydrodechlorination of aryl chlorides catalyzed by [Cp*₂RhCl₂]₂ and related complexes using refluxing 2-butanol as solvent and hydrogen source in the presence of bases. The system showed high compatibility with functional groups.

Intriguing transition-metal complex/NHC/alkoxide systems (NHC = *N*-heterocyclic carbene) have been applied recently for haloarene reduction. Nolan and coworkers [107] have found that SIMes·HCl ((2,4,6-trimethylphenyl)dihydroimidazolium chloride) is the most effective of the NHC precursors when combined with [Pd(dba)₂] for the dehalogenation of mono- and polyhalogenated arenes at 100 °C in dioxane. Strong bases having β-hydrogens both performed deprotonation of the imidazolium salt and behaved as hydrogen sources. Very recently, these authors have used a series of air- and moisture-stable [(NHC)Pd(allyl)Cl] complexes for dehalogenation processes with microwave assistance (120 °C) or with conventional heating (60 °C) affording very high yields in both cases [108]. In related studies, Fort and associates [109] have applied [Ni(acac)₂] as a catalyst. The complex associated to IMes·HCl (1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride) and *in-situ*-generated *i*-PrONa in refluxing THF proved to have high efficiency and functional group tolerance in the reduction of various mono- and polyhalogenated arenes.

Water-soluble transition-metal complexes have been used recently for transfer hydrogenolysis of halocarbons. Paetzold and Oehme [110] have realized the reductive dehalogenation of allyl or benzyl halides in the presence of [(phosphine)₂PdCl₂] complexes with sulfonated phosphines as ligands (e.g., Ph₂P(CH₂)₃SO₃K) by

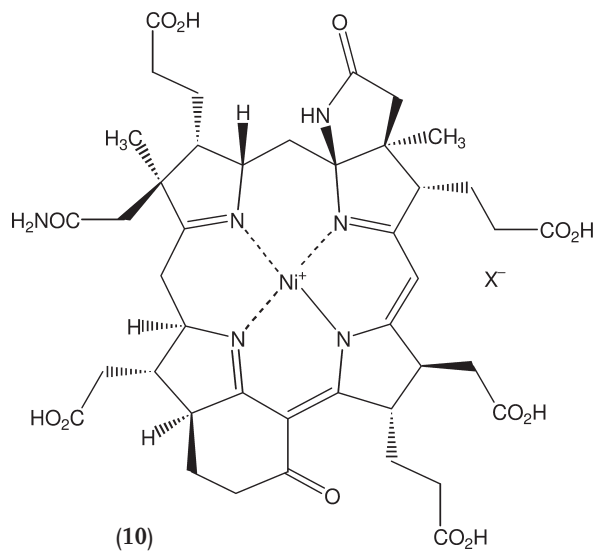
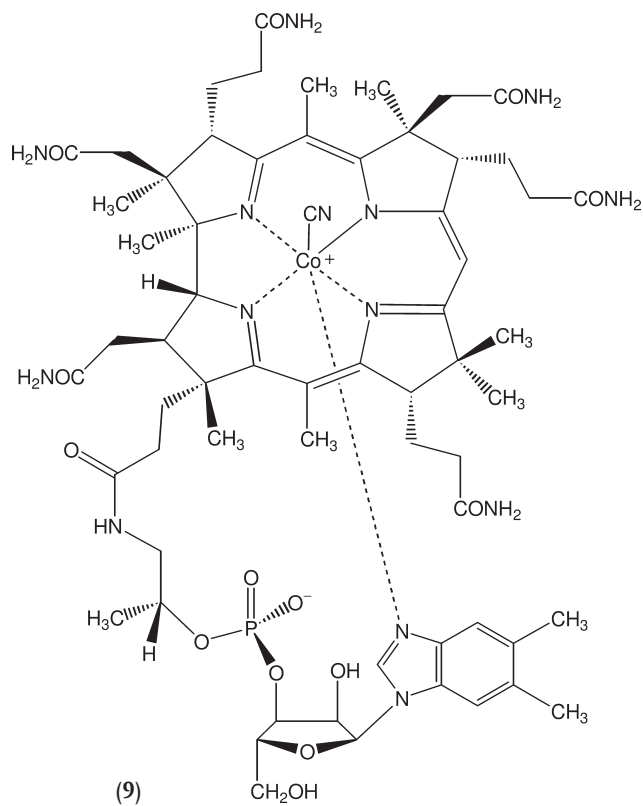
means of formates in a biphasic water/heptane system at 90 °C. This reaction could be promoted by addition of polyethers of different types as phase-transfer agents, the best results being obtained with triethylene glycol. Joó and associates [111] catalyzed the transformation of C–X bonds into C–H bonds by water-soluble Ru(II) phosphine complexes. CCl₄ was converted into CHCl₃ and CH₂Cl₂. Excellent TOFs up to 1000 h⁻¹ could be achieved at 80 °C when, for example, an aqueous solution of HCOONa was the hydrogen donor and [(TPPMS)₂RuCl₂] the catalyst (TPPMS = *m*-sulfophenyldiphenylphosphine Na salt) (see Table 18.3). Ogo, Watanabe and colleagues [112] have reported a pH-dependent transfer dehalogenation of water-soluble substrates with organoiridium(III) aqua complexes such as [Cp*Ir(bpy)(H₂O)]²⁺ (**8**) as catalyst precursors and formates as hydrogen donors. For example, **8** reacted with the formate ions at pH 5.0 to form the hydride [Cp*Ir(bpy)(H)]⁺, which acted as active catalysts in the hydrogenolysis of 2- and 3-halopropanoic acids.

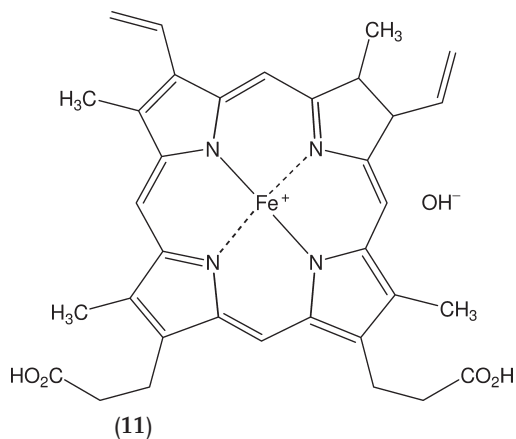
Perfluoroaromatic Grignard reagents (R_FMgBr) were formed from alkylmagnesium bromides and perfluoroarenes in the presence of transition-metal halides (mainly CoCl₂) as catalysts in THF at about 0 °C, as had been reported during the late 1960s. Hydrolysis of the reaction mixtures resulted in the formation of R_FH [113]. Colomer and Corriu have applied the system [Cp₂TiCl₂]/*i*-PrMgBr in Et₂O for debromination, and *p*-BrC₆H₄Cl gave chlorobenzene selectively [114]. Deiodination and debromination of aromatic halides proceeded smoothly with high yields when treated with RMgX (where R groups have β-hydrogens) and a catalytic amount of [Cp₂ZrCl₂] [115]. From [Cp₂TiCl₂] and the above type of Grignard reagents, an effective catalyst system was obtained even for dechlorination [116]. Addition of [(dppf)PdCl₂] or [(dppf)Pd] markedly accelerated the reduction of alkyl halides with Grignard reagents in Et₂O, but in THF the reduction was independent of palladium [117]. Benzyl halides underwent halogen/hydrogen exchange with equimolar amounts of Et₂Zn in DMF at room temperature using [(PPh₃)₄Pd] as a catalyst. The method tolerated a variety of functional groups [118]. Very recently, Kotora and coworkers [119] have developed iron- and ruthenium-containing catalytic systems capable of reductive dehalogenation of 2-chloro-*α,ω*-dienes when combined with trialkylaluminum reagents.

18.2.5

Biomimetic Dehalogenations

Halocarbons are common soil, sediment, and groundwater pollutants, many of them being toxic, mutagenic materials [6, 120]. Although certain anaerobic microorganisms are capable of reductively degrading halocarbons, these processes are often slow, and high pollutant concentrations may be toxic, even for the bacteria. Thus, the problem of toxicity may be eliminated rather by biomimetic catalysis than by biocatalysis [121]. Reduction of organic halides has been investigated in the presence of transition metal-containing coenzymes vitamin B₁₂ (Co, **9**), F₄₃₀ (Ni, **10**), hematin (Fe, **11**), and related complexes. In the most cases, corrinoids have been applied (for earlier results, see [122]).

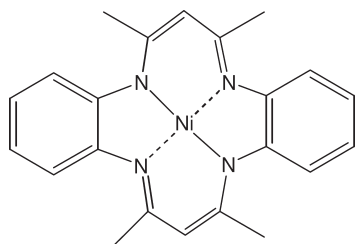




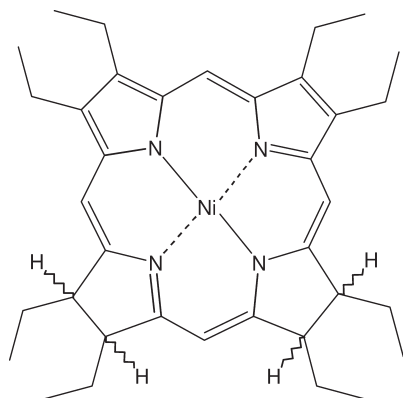
It should be emphasized that the aim of the great part of these biomimetic studies was *degradation* of the substrate and not the halogen/hydrogen exchange resulting in one or more product(s). This concerns above all the detoxification of polyhalogenated methanes and related pollutants (cf. [123–127]). The product composition depends strongly on the reducing agents: Ti(III) citrate [121, 128–131], dithiothreitol [121, 130], cysteine, and sulfides [130, 132, 133] have been used most frequently. The results of Morra and colleagues [130] may serve as an example. They catalyzed the dehalogenation of CCl_4 with corrins (vitamin B_{12} , cobinamide dicyanide, or aquocobalamin). Products in the presence of Ti(III) citrate were mostly hydrogenolytic and included predominantly CH_3Cl and CH_4 , whereas they were CH_2Cl_2 , CO and formate in the case of dithiothreitol. Sulfide/cysteine reductants were least reactive against CCl_4 , giving the major products CHCl_3 , CS_2 , 2-oxothiazolidine carboxylic acid, and 2-thioxo-4-thiazolidinecarboxylic acid. In addition to cobalt complexes, a pyridine-2,6-bis(thiocarboxylic acid)-Cu(II) complex [134], and an iron porphyrin in the presence of cysteine [135, 136] have been found to be active in the degradation of CCl_4 and related compounds.

Vitamin B_{12} catalyzed also the dechlorination of tetrachloroethene (PCE) to trichloroethene (TCE) and 1,2-dichloroethene (DCE) in the presence of dithiothreitol or Ti(III) citrate [137–141], but zero-valent metals have also been used as bulk electron donors [142, 143]. With vitamin B_{12} , carbon mass recoveries were 81–84% for PCE reduction and 89% for TCE reduction; *cis*-1,2-DCE, ethene, and ethyne were the main products [138, 139]. Using Ni(II) humic acid complexes, TCE reduction was more rapid, leading to ethane and ethene as the primary products [144, 145]. Angst, Schwarzenbach and colleagues [140, 141] have shown that the corrinoid-catalyzed dechlorinations of the DCE isomers and vinyl chloride (VC) to ethene and ethyne were pH-dependent, and showed the reactivity order: 1,1-DCE > VC > *trans*-DCE > *cis*-DCE. Similar results have been obtained by Lesage and colleagues [146]. Dror and Schlautmann [147, 148] have demonstrated the importance of specific core metals and their solubility for the reactivity of a porphyrin complex.

Several research groups have investigated catalytic systems related to F_{430} . Gantzer and Wackett [149] have found different reactivity orders for the substrates examined: in the case of vitamin B_{12} (**9**) and coenzyme F_{430} (**10**), $CCl_4 > C_2Cl_4 > C_6Cl_6$, for hematin (**11**), $CCl_4 > C_6Cl_6 > C_2Cl_4$. TCE was dechlorinated stereoselectively to *cis*-1,2-dichloroethene with **9–11**. Arai and colleagues [150] catalyzed efficiently the hydrodehalogenation of cycloalkyl halides yielding cycloalkanes by $[Ni(tmtaa)]$ (**12**; tmtaa = dianion of 6,8,15,17-tetramethyl-5,14-dihydro-dibenzo[*b,i*][1,4,8,11]tetraaza-cyclotetradecine) in combination with $NaBH_4$ or $NaBH(OMe)_3$ under mild conditions.



(12)



(13)

Stolzenberg's group [151–153] has studied the ability of various nickel(II) macrocycle and coordination complexes (e.g., **7**, **10**, and $[Ni(OEiBC)]$ (**13**; OEiBC = octaethylisobacteriochlorin, mixture of isomers)). The facility of catalytic reduction of cyclohexyl bromide by $NaBH_4$ varied markedly with the structure of the ligands and the solvent composition. The highest TOFs (up to 70 h^{-1}) were obtained by the complex **7** (see Section 18.2.2) in diglyme/ethanol. Morra and coworkers [154] have shown that a combination of aquocobalamin or **10** and $Fe(0)$ may effectively promote dehalogenation.

18.2.6

Electrochemical Reductions

Electrochemical methods are available for the direct dehalogenation of organic halides to a limited extent: fluorides and monochlorides are generally not reducible [1]. In the presence of transition-metal complexes as mediators (Med), however, the electrolysis of halocarbons (RX) can be performed more effectively and selectively under various conditions [155–158]. Mediated electroreduction is most efficient when the electron transfer step E° (Med/Med $^{\bullet-}$) is more negative than E° (RX/RX $^{\bullet-}$) [157] (cf. Section 18.4.1).

Pletcher and associates [155, 159, 160] have studied the electrochemical reduction of alkyl bromides in the presence of a wide variety of macrocyclic Ni(II) complexes. Depending on the substrate, the mediator, and the reaction conditions, mixtures of the dimer and the disproportionation products of the alkyl radical intermediate were formed (cf. Section 18.4.1). The same group [161] reported that traces of metal ions (e.g., Cu $^{2+}$) in the catholyte improved the current density and selectivity for several cathodic processes, and thus the conversion of trichloroacetic acid to chloroacetic acid. Electrochemical reductive coupling of organic halides was accompanied several times by hydrodehalogenation, especially when Ni complexes were used as mediators. In many of the reactions examined, dehalogenation of the substrate predominated over coupling [162–165].

The use of electrochemical methods for the destruction of aromatic organochlorine wastes has been reviewed [157]. Rusling, Zhang and associates [166, 167] have examined a stable, conductive, bicontinuous surfactant/soil/water microemulsion as a medium for the catalytic reduction of different pollutants. In soils contaminated with Arochlor 1260, 94% dechlorination was achieved by [Zn(pc)] (H $_2$ pc=phthalocyanine) as a mediator with a current efficiency of 50% during a 12-h electrolysis. Conductive microemulsions have also been employed for the destruction of aliphatic halides and DDT in the presence of [Co(bpy) $_3$] $^{2+}$ (bpy=2,2'-bipyridine) [168] or metal phthalocyanine tetrasulfonates [169].

Nünnecke and Voss [158] reduced aryl chlorides electrochemically in methanol using [(bpy)NiCl $_2$] and [(cyclam)NiCl $_2$] (cyclam=1,4,8,11-tetraazacyclotetradecane) as mediators. More highly chlorinated benzenes were converted to chlorobenzene, whereas chlorodibenzofurans gave unsubstituted dibenzofuran as the major product. Due to the mediators, higher selectivities could be achieved, and the formation of hydrogenated products was completely suppressed. Peters and associates [170–174] have applied electrogenerated Co(I) salen (H $_2$ salen=bis(salicylidene)ethylenediamine) or Co(I) salophen (H $_2$ salophen=bis(salicylidene)-1,2-phenylenediamine) for the catalytic reduction of various halogenated substrates. In the case of 1,1,2-trichloro-1,2,2-trifluoroethane, cyclic voltammetry and controlled-potential electrolysis resulted in the formation of CFCl=CF $_2$ and CF $_3$ CH $_2$ F as main products, respectively, using DMF as a solvent and Bu $_4$ NBF $_4$ as a supporting electrolyte [174]. Mugnier, Harwey and coworkers [175, 176] activated the C–Br and the C–I bonds by the cluster [(dppm) $_3$ Pd $_3$ (CO)] $^{2+}$ (dppm=bis(diphenylphosphino)-

methane). Catalytic dehalogenation of 2,3,4-tri-*O*-acetyl-5-thioxylopyranosyl bromide (Xyl-Br, both α - and β -isomers) provided Xyl-H as the major organic product at the potential of -0.9 V (versus SCE).

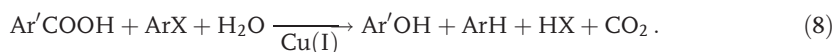
18.2.7

Miscellaneous Reducing Methods

Martin and associates [124, 125] have studied the dehalogenation of CHCl_3 in boiling methanol by Schiff-base complexes of some transition metals in the presence of TMEDA. The kinetics of chloride ion formation has been measured without characterizing the organic products. Nahar and Mukhedkar [126, 127] found that the reactivities of related Schiff-base complexes in the above reaction decreased in the order $\text{Pd} > \text{Pt} > \text{Ni} > \text{Cu} > \text{Zn}$.

Several researchers hydrogenolyzed – mostly activated – alkyl halides under carbonylation conditions and/or in the presence of metal carbonyls. Alper and coworkers debrominated bromomethyl ketones with $[\text{Co}_2(\text{CO})_8]$ as a catalyst under phase-transfer conditions [177]. Brunet and Taillefer [178, 179] catalyzed the reduction of aryl iodides by *in-situ*-generated $\text{K}[\text{HFe}(\text{CO})_5]$ in methanol (up to 18 cycles) under 0.1 MPa CO pressure at 60°C ; several functional groups were tolerated. An intriguing method has been developed by Cavinato and Toniolo [180] for the synthesis of γ -keto acids of the type $\text{ArC}(\text{O})\text{CH}_2\text{CH}_2\text{COOH}$ via carbonylation-decarboxylation of $\text{ArC}(\text{O})\text{CH}_2\text{CHClCOOH}$. The reactions were carried out in the presence of Pd(II) phosphine complexes, typically at 2–3 MPa CO and 100 – 120°C in acetone/ H_2O . When the same authors [181] attempted the carbonylation of 2-chlorocyclohexanone with the system $[(\text{PPh}_3)_2\text{PdCl}_2]/\text{PPh}_3/\text{EtOH}/\text{H}_2\text{O}$ (at 100°C and 10 MPa CO, $\text{P}/\text{Pd}=2.5$), a hydrogen transfer occurred leading to halogen/hydrogen exchange. Trabuco and Ford [182] have shown that homogeneous catalysts prepared from RhCl_3 in aqueous aromatic amines reduce C–Cl bonds under mild water gas shift conditions (100°C and 0.1 MPa CO). In a 4-picoline/ H_2O solvent mixture, 1,2-dichloroethane was transformed to ethene and ethane. An ambient temperature liquid carbonylmetallate, $[\text{bmim}][\text{Co}(\text{CO})_4]$ ($[\text{bmim}]^+ = 1$ -butyl-3-methylimidazolium cation), has been prepared by Dyson and coworkers [183]. The mixture of the ionic liquid and NaOH catalyzed the debromination of 2-bromoketones.

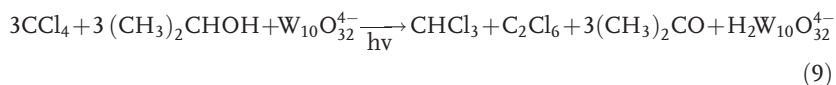
An interesting new homogeneous catalytic process was developed by Buijs [184] for the reductive dehalogenation of polychlorinated and -brominated aromatic hydrocarbons and ethers. Cu(I) benzoate catalyzed the reaction under Dow-Phenol conditions in the absence of air at 235°C (Eq. (8)):



Starichenko and colleagues [185–187] have studied the hydrogenolysis of polychloro- and polyfluoroaromatic compounds with the $[(\text{N}\cap\text{N})\text{NiCl}_2]/\text{Zn}$ reducing system ($\text{N}\cap\text{N} = \text{bpy}$ or phen (phen = 1,10-phenanthroline)). Using DMF or DMA

solvents in the presence of water or NH_4Cl , the displacement of the Cl or F atoms by H took place at 50–70 °C. Interestingly, the systems catalyzed the regioselective *ortho*-hydrodefluorination of pentafluorobenzoic acid to 2,3,4,5-tetrafluorobenzoic and 3,4,5-trifluorobenzoic acids in high yields [187].

The applications of polyoxometalates in catalytic dehalogenation of halocarbons have been succinctly reviewed by Hill and coworkers [188]. This reaction involves the photocatalytic transformation of organic halides coupled with the oxidation of sacrificial organic reductants (secondary alcohols or tertiary amides) (Eq. (9)) [189, 190]:



Very recently, Gkika and colleagues [191] realized the degradation of diversified pesticides (e.g., lindane) to CO_2 , H_2O and the corresponding inorganic anions by photolysis in the presence of polyoxotungstates. A stable “hydrophobic vitamin B_{12} ”, heptamethyl cobyrinate perchlorate catalyzed efficiently the reduction of DDT using a visible light irradiation system containing a $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ photosensitizer [192].

18.3

Mechanistic Considerations

The mechanisms of the homogeneous catalytic hydrodehalogenation have been examined by the following methods:

- spectroscopic investigations to detect intermediates in the reaction mixtures;
- isolation and characterization of possible intermediates or related model compounds;
- qualitative and quantitative analysis of the organic products;
- kinetic measurements; and
- systematic variation of the structure of the substrate and/or the catalyst. Theoretical investigations (e.g., MO calculations) have also been made.

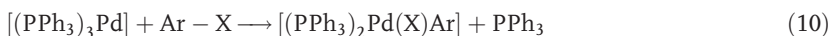
In spite of the wide variety of substrates, hydrogen sources, and catalysts applied in the hydrodehalogenations of organic halides, some general statements can be made on the reaction pathways. We shall examine the following crucial steps of the dehalogenations: activation of the C–X bond, steps involving the reducing agents, and formation of the products.

18.3.1

Activation of the C–X Bond18.3.1.1 **Oxidative Addition**

This type of activation may proceed by various mechanisms, which have been discussed exhaustively [2, 193, 194].

S_N2 and S_NAr Reactions In these reactions the metal atom attacks aliphatic or aromatic carbon bonded to X, respectively. A stronger nucleophilic metal as well as a better leaving group X (I > Br > Cl > F) facilitates, whereas steric hindrance in R slows these types of oxidative addition [193, 194]. S_NAr reactions are favored by electron-withdrawing substituents Y in the case of the substrates 4-YC₆H₄X [2]. S_N2 [27, 29, 89, 117, 180, 181] and S_NAr [31, 33, 62–67, 95, 100, 107–109] mechanisms have been suggested frequently for zerovalent d¹⁰ complexes such as [L_nM] (M = Ni, Pd, Pt; L = tertiary phosphine; n = 2, 3, 4). For example:

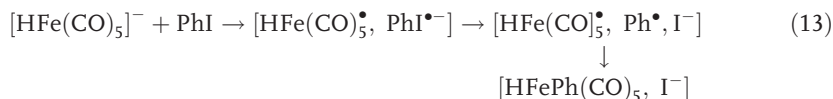


Products of S_NAr-type oxidative additions in some active Pd- or Ni-containing hydrodehalogenating systems have been isolated and characterized structurally (e.g., [(PEt₃)₂NiCl(*p*-C₆Cl₅C₆Cl₄)] [31], [(PPh₃)₂PdBr(3,4,5-tribromo-2-thienyl)] [62]). The reactivity order Ni > Pd > Pt has been found for the oxidative addition of aryl halides. Steric and electronic properties, and the numbers of L as well as chelate effects, play an important role [65, 194–196]. For example, Pd(0) complexes of basic chelating phosphines react substantially more easily with chlorobenzenes than their nonchelating analogues (see Section 18.2.4) [2, 100, 196]. In contrast to [L_nPd], oxidative addition of aryl halides on [L_nNi] often proceed by single electron transfer mechanism [2, 197]. S_N2 and S_NAr types of oxidative addition as a step of the catalytic dehalogenation have also been proposed in the literature for low-valent Ti [40, 114], Zr(II) [115], Ru(II) [20, 74, 81, 98], Rh(I) [18, 29, 68, 81, 91] and Pt(II) [82, 83] complexes.

Atom Transfer Atom Transfer (AT) takes place typically in the case of d⁷ complexes, which abstract the halogen atom from RX. The radical formed combines then with a second metal [193, 194]. A “classical” example of this mechanism is the hydrodehalogenation with cyanocobaltates(II) (see Section 18.2.1) [8, 9], but an analogous pathway was suggested recently for the Co(II) corrin-catalyzed dechlorination of CCl₄ in the presence of S²⁻/cysteine as reductant (Eqs. (11)–(12)) [130]:



Single Electron Transfer A single electron transfer (SET) mechanism is often difficult to distinguish from an S_N2 reaction because the principal product of these two pathways is the same, apart from the stereochemistry at carbon (racemization instead of inversion). The radicals formed can recombine rapidly in a solvent cage (*inner-sphere ET*) [2, 193, 194]. The $[\text{HFe}(\text{CO})_5]^-$ -catalyzed deiodination of iodobenzene may serve as an example [179] (Eq. (13)).

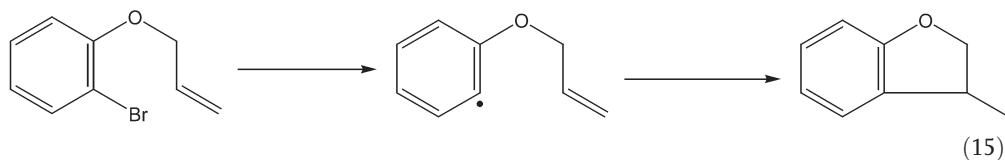


Coordinatively unsaturated complexes and those giving easily such species by ligand dissociation favor pathways related to that described in Eqs. (10) and (13). Coordinatively saturated complexes reduce halocarbons via *outer-sphere ET* [193, 194]. In cases of electrochemical dehalogenations, the species formed by one-electron reduction of the mediators on the cathode often react in this way [156, 157, 198]. For example (Eq. (14)) [157, 166]:



A SET process has been postulated between Rh(III) oxidative adducts and an NAD(P)H model compound (cf. Section 18.2.4) [91]. Oxidative adducts formed by S_N2 , $S_N\text{Ar}$, or inner-sphere SET pathways may produce radicals by homolytic M–C bond cleavage [130, 155, 176, 199].

The transformation of the radical (R^\bullet) (which may escape also from the solvent cage) affords several products. Usually, RH is formed by hydrogen abstraction from the reducing agent or the solvent [36, 91, 150, 157, 169, 173, 179, 198], but dimerization [173, 194, 198], disproportionation (formation of RH and R(–H) simultaneously) [155, 158–160, 170], or rearrangement [43, 49, 55, 165, 194] can also take place. For example, the formation of the cyclized product in the reaction of Eq. (15) requires the intermediacy of an aryl radical [49, 55]:

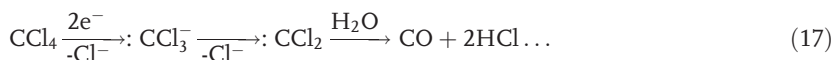


The C–F bond activations in C_6F_6 and related compounds with ruthenium [200, 201] and rhodium [17, 78, 201] complexes, for which an $S_N\text{Ar}$ mechanism is energetically unfavorable, have been explained by SET pathways. Both S_N2 [128, 129, 131, 170–174, 199, 202] and SET [130, 132, 199] mechanisms have been proposed for the reaction of Co(I) complexes with alkyl and vinyl halides.

Carbanions may be formed in the electrochemical reductions of aryl halides [157, 158] (Eq. (16)):



and of *gem*-di- or trihaloaliphatics [174, 198], as well as in the hydrogenolysis of the latter type of substrates with corrinoids and related complexes [130, 199, 203]. The cleavage of a halide ion from a polyhalocarbanion (or from its complex) affords (di)halocarbene (or its complex) which will be transformed depending on the reaction conditions [130, 203, 204]. Equation (17) shows some of the possible transformations of CCl_4 in the presence of corrins [130]:



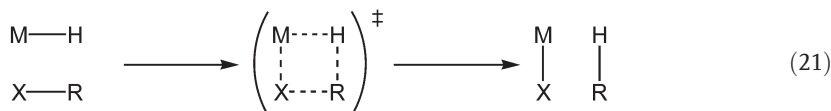
Radical Chain Mechanism This mechanism also requires a coordinatively unsaturated metal and the presence of a radical initiator Q^\bullet (trace of O_2 , $h\nu$, etc.). Such a pathway has been proposed for a Ni(II) complex-catalyzed dehalogenation of polyhaloarenes [60], and it occurs frequently in the stoichiometric C–X activations with early transition-metal complexes (see [205–207]).



In addition to initiation (Eq. (18)) and propagation (Eqs. (19) and (20)), termination steps are also possible (resulting in, for example, dimers of R^\bullet). Radical traps inhibit this type of oxidative addition [194].

18.3.1.2 σ -Bond Metathesis

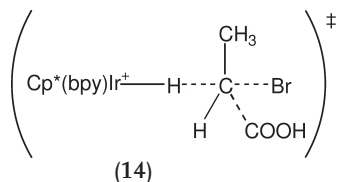
This is the simultaneous breaking and formation of bonds to the metal with a four-membered ring transition state (Eq. (21)):



This concerted process may operate in the case of d^0 early metal complexes where the oxidative addition is forbidden [194]. Nevertheless, it was postulated also in the interaction of a dihalo-ruthenium(II) intermediate and a hydrosilane [74].

18.3.1.3 S_N2 Attack of the Hydride Ligand

Another route not involving an M–C bond formation has been suggested recently for some water-soluble Ir(III) complexes [112]. The hydride pushes the halide from the carbon atom directly by an S_N2 way with the 14 transition state.



18.3.1.4 1,2-Insertion

1,2-Insertion of the C=C bond into an M–H bond precedes frequently the C–X bond activation in halogenated alkenes. Such a pathway has been suggested for the cobalamin-mediated dechlorinations of *cis*- and *trans*-DCE, as well as VC with Ti(III) citrate as a reducing agent [141].

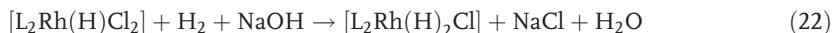
18.3.2

Reaction Steps Involving the Reducing Agents

The double role of the reducing agents in homogeneous hydrodehalogenations is:

- (i) transformation of the transition-metal complex into a state capable of the activation of the substrate;
- (ii) formation of the M–H bond to cleave – directly or indirectly – the C–X bond of the substrate [3, 208].

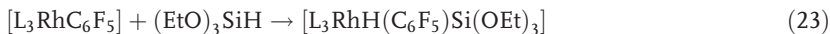
Processes corresponding to both of these roles are not involved by all means in each catalytic cycle. They may also take place in one step [24, 74]. Process (i) is needed generally to transfer – mostly to reduce – the precursor complex into a catalytically active form. Reactions related to that of Eq. (22) (L = PCy₃, Pi-Pr₃ [13]) are promoted by the addition of bases [2, 20, 24, 28, 29, 45, 47, 65, 106, 108]:



In outer-sphere SET reductions (e.g., in electrochemical dehalogenations), hydrogen abstraction by R[•] leads to the product RH (i.e., no step related to (ii) is required to occur). Process (ii) follows generally the activation of the substrate in the proposed hydrodehalogenation cycles, but we know also of opposite examples [77, 82, 106, 112].

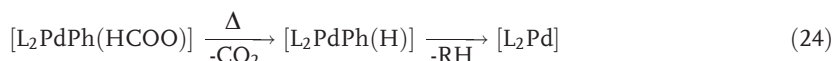
The nature of the M–H bond-forming step, (ii), in a given catalytic cycle depends strongly on the reducing agent used. Dihydrogen [13, 14, 17, 20, 24, 29] and hydrosilane [78, 81, 82] react mostly by *oxidative addition* [193, 209, 210]. For example, the product of the reaction in Eq. (23) – which is involved in an

actual “working” catalytic cycle – has been isolated and characterized by its X-ray structure (L=PMe₃) [78]:



The *heterolytic activation* of H₂ has been considered in systems containing basic ligands such as pyridine [18, 29, 209]. *Transmetalation* proposed for Bu₃SnH as a reductant resulted in the transformation of the Pd–Br bond into Pd–H [89].

Simple and complex metal hydrides as strong nucleophiles easily displace the halide bound to the central atom of the catalyst by *hydride transfer* [40, 45, 62–67]. Alcoholates [97, 98, 100, 106, 108], formates [93, 96, 100, 112], and metal alkyls [114, 115, 117] also substitute the halogen atom on the transition metal, after which the hydrogen transfer takes place from the alkoxy, formate and alkyl ligands formed [3, 211]. A good model for the halobenzene reduction catalyzed by the [L_nPd]/HCOO[−] system [98, 100, 112] has been found by Alper and co-workers [211]. Decomposition of the organopalladium formate complex, [(PPh₃)₂PdPh(HCOO)], gave benzene, indicating the intermediacy of a Pd–H species (Eq. (24), L=PPh₃) [211]:

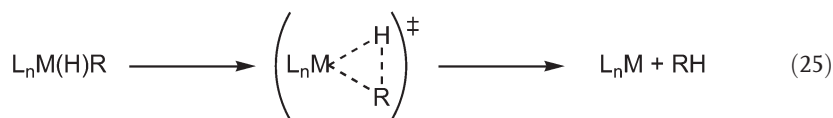


18.3.3

Formation of the Product

The product-forming steps of dehalogenations by free radical pathways were discussed earlier (see Section 18.3.1.1). In non-radical mechanisms, the dehalogenated products (RH) will be formed mostly by reductive elimination [193, 194]; however, concerted processes lead directly from RX to RH (see Sections 18.3.1.2 and 18.3.1.3).

Catalytic dehalogenation cycles with a binuclear reductive elimination step have not yet been reported, but many examples are known with a single metal. The RH product eliminates easily from d⁸ metals (Ni(II), Pd(II)) or d⁶ metals (Ru(II), Rh(III)) (Eq. (25)) [196]. This reaction is believed to go by a three-center transition state [193, 194, 212]:



In the case of R=aryl with electron-withdrawing substituents, however, kinetic measurements indicated a rapid, reversible η²-arene complex formation followed by the rate-determining loss of the arene [213].

Since the reaction in Eq. (26) is generally the last step of the catalytic cycle, the $[L_nM]$ fragment should survive long enough to react with the substrate again. The presence of an excess of phosphine ligand can facilitate the reductive elimination and can also stabilize the $[L_nM]$ species [3, 194].

18.4

Concluding Remarks

Our knowledge regarding transition metal-mediated (catalytic and stoichiometric) hydrodehalogenation has advanced significantly during the past two decades. One favorable aspect of this progress is that such progress has been achieved mainly in the activation of the more stable C–Cl and C–F bonds. In the former case, environmental concerns have dominated, including the detoxification of chlorocarbon pollutants by biomimetic, electrochemical and other methods in solving problems caused by chemical industrial processes. From the synthetic viewpoint, the most intriguing results have been achieved in fluorine/hydrogen exchange, as in addition to stoichiometric transformations a number of catalytic processes have also been developed. In the near future, a step-up in the efficiency of the homogeneous hydrodehalogenation – that is, increasing the turnovers under the mildest possible reaction conditions – appears to be a real possibility, both in environmental and synthetic applications.

Acknowledgments

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Abbreviations

γ -AMP	γ -aminopropyl
BNAH	<i>N</i> -benzyl-1,4-dihydronicotinamide
CFC	chlorofluorocarbon
DCE	1,2-dichloroethene
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
HCFC	hydrochlorofluorocarbon
NHC	<i>N</i> -heterocyclic carbene
OEiBC	octaethylisobacteriochlorin
PCB	polychlorinated biphenyl
PCE	tetrachloroethene

PHMS	polymethylhydrosiloxane
SCE	standard calomel electrode
SET	single electron transfer
TCE	trichloroethene
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TOF	turnover frequency
TON	turnover number
TPPMS	<i>m</i> -sulfophenyldiphenylphosphine
VC	vinyl chloride

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