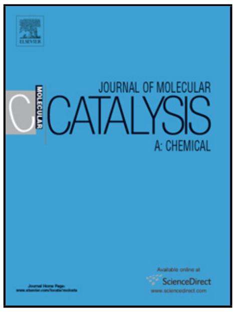

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Dehalogenation of organic halides in aqueous media by hydrogen transfer from formate catalyzed by water-soluble Ru(II)-N-heterocyclic carbene complexes

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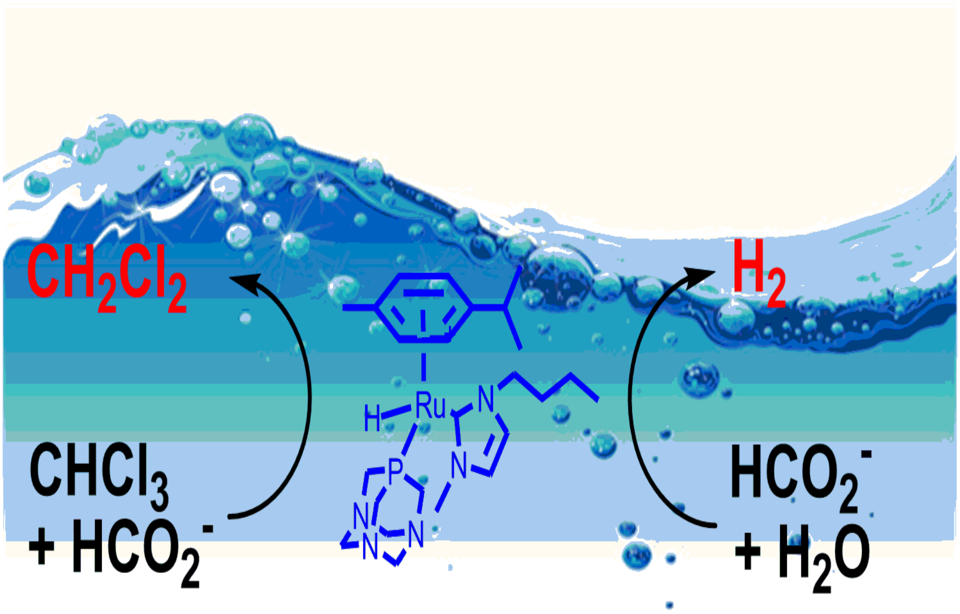
Graphical abstract



Highlights

- Organic halides were hydrodehalogenated by homogeneous catalysis in aqueous system
- Dehalogenations proceeded by hydrogen transfer from aqueous sodium formate
- Water-soluble, mixed-ligand NHC-posphine-Ru(II) catalysts were employed
- A catalytic cycle is proposed on basis of kinetic and NMR measurements

Abstract:

Water-soluble [RuCl(NHC)(L)(η^6-arene)] complexes (NHC = bmim = 1-butyl-3-methyl-imidazole-2-ylidene; L = tertiary phosphine, such as *m*tppms, *m*tppts, pta, pta-Me and pta-Bn; η^6-arene = η^6-*p*-cymene) were succesfully applied for the first time as catalysts in hydrodehalogenation of organic halides by hydrogen transfer from aqueous Na-formate with turnover frequencies up to TOF=112 h^{-1} at 80°C. Simultaneous to hydrodehalogenation, aqueous formate was also decomposed to H_2 and HCO_3^-. In case of [RuCl(bmim)(pta)(η^6-*p*-cymene)]Cl (pta =1,3,5-triaza-7-phosphaadamantane) a reaction mechanism is suggested on basis of kinetic and NMR measurements which accounts for both hydrodehalogenation and formate dehydrogenation and involves [RuH(bmim)(pta)(η^6-*p*-cymene]$^+$ as the key catalytic species for both cycles.

Keywords: hydrodehalogenation; formate dehydrogenation; N-heterocyclic carbene complexes; ruthenium; water-soluble

1. Introduction

Reductive dehalogenation of organic halides plays important role in synthetic chemistry as well as in chemical destruction of halogen-containing organic pollutants [1-8]. Homogeneous catalytic methods apply metal complexes based mostly on palladium [8-16], however, complexes of ruthenium [17-22], rhodium [20, 22-27], cobalt and nickel [28] are also found among the most active catalysts. It is of interest in this regard, that the extensively studied various C-C coupling reactions with organic halides as one of the reactants also imply catalytic rupture of the C-Halogen bond; it comes as no surprise that palladium complexes are most often featured as catalysts of choice in C-C couplings, too. In addition to H_2, other hydrogen donors, such as silanes [4, 17, 29], and formates [14, 28] have also been used. For example, Na-formate dissolved in 2-propanol was found to be a very efficient hydrogen donor in dehalogenations of hexachlorocyclohexane and hexachlorobenzene catalyzed by Rh(I)-complexes [25].

Traditionally, tertiary phosphine complexes play important role in hydrodehalogenations. Nevertheless, in the last two decades N-heterocyclic carbene (NHC) complexes were introduced into many areas of organometallic catalysis [30, 31]. NHC ligands (such as e.g. imidazole-2-ylidenes) form stable bonds to transition metal ions and the resulting complexes become suitable for application as catalysts under harsh conditions (at high temperatures, in the presence of strong bases, etc), too. Typical reactions which include transition metal NHC complexes are C-C couplings, olefin metathesis, cycloadditions, hydroformylation, hydrogenation, transfer hydrogenation, redox isomerization, hydrosilylation, hydration, etc. [32]. N-heterocyclic carbene complexes were used in hydrodehalogenations [10-13], as well, and were found promising in catalysis of the usually difficult reductive defluorination reactions, too [7, 33].

Application of transition metal NHC complexes in aqueous catalysis has expanded enormously in the last 10 years, so much that it was covered by three extensive reviews [34-36]. Water as solvent has many attractive features in organic and organometallic chemistry [37, 38]. Certainly, the main impetus comes from the possible elimination of hazardous organic solvents (the green aspect) although treatment of polluted wastewater also needs serious attention. Hydrodehalogenation in aqueous systems was rarely reported, one example being the slow ($TOF<6.3\ h^{-1}$; $TOF=mol\ reacted\ substrate\times(mol\ catalyst\times time)^{-1}$) dehalogenation of water-soluble chloro- and bromopropanoic acids by aqueous Na- and NH_4-formates catalyzed by various Cp*Ir complexes [39]. In another study, Bényei et al [19] reported a very efficient system for hydrodehalogenation of alkyl, benzyl, and aryl halides using water-soluble Ru(II)-phosphine complexes as catalysts for hydrogen transfer from aqueous Na-formate; the initial TOF of $CHCl_3$ dehalogenation reached 1000 h^{-1}. However, hydrodehalogenation in aqueous media catalyzed by water-soluble transition metal NHC complexes has not been reported so far.

For several years, we have been interested in syntheses of water-soluble organometallic complexes and their catalytic applications in aqueous solutions or aqueous-organic biphasic systems [37, 40-44]. Here we report the first successful application of water-soluble Ru(II)-NHC-phosphine complexes as catalysts for hydrodehalogenation of organic halides in aqueous systems with hydrogen transfer from Na-formate. The catalysts were obtained in reactions of $[RuCl_2(bmim)(\eta^6\text{-}p\text{-cymene})]$ [40] and various water-soluble phosphine ligands shown on Scheme 1. Reactions catalysed by one of these complexes, $[RuCl(bmim)(pta)(\eta^6\text{-}p\text{-cymene})]Cl$ (pta=1,3,5-triaza-7-phosphaadamantane=1,3,5-triaza-7-phosphatricyclo[3.3.1.1]^{3,7}decane) were studied in detail. It was found, that in addition to hydrodehalogenation this complex also catalyzed the decomposition of aqueous formate to H_2 and HCO_3^-, too. On basis of kinetic studies, a possible mechanism for the simultaneous hydrodehalogenation and formate dehydrogenation is also suggested.

2. Experimental

2.1 Materials, general instrumentation and procedures

All commercial reagents were high purity products of Sigma Aldrich and were used as received. $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2]$ [45], and the water-soluble phosphines, *m*tppms-Na [46], *m*tppts-Na_3 [47], pta [48], [pta-Me](OSO_2CF_3) [49], and [pta-Bn]Cl [50] were prepared according to known methods. $[RuCl_2(bmim)(\eta^6\text{-}p\text{-cymene})]$ was prepared from $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2]$ and 1-butyl-3-methylimidazolium chloride, [bmim]Cl by the silver-carbene transfer methodology as described earlier [40]; ^1H and ^{13}C NMR spectra of the product were identical to those in the literature.

^1H, ^{13}C, and ^{31}P NMR spectra were recorded by Bruker 400 MHz and Bruker 360 MHz NMR spectrometers and referenced to DSS (4,4-dimethyl-4-silapentane-1-sulfonic acid sodium salt), TMS (tetramethylsilane), 85% phosphoric acid, and residual solvent peaks, respectively. For elemental analyses an ElementarVario Micro (CHNS) equipment was used. ESI-MS data were collected on a BRUKER BioTOF II ESI-TOF spectrometer in positive ion mode.

Gas chromatographic analysis of hydrodehalogenation reaction mixtures were done by using an Agilent 7890A equipment (automatic injector; column: MN Optima® -1, 0.25 µm x 30 m x 0.32 mm; carrier gas: N_2; injector at 280°C; FID at 300°C). Sensitivity of the detector for all substrates and their dehalogenation products was calibrated using naphthalene as internal standard. The Agilent Data System program was used for data collection and analysis.

2.2 General procedure of the dehalogenation

Hydrodehalogenation reactions were run with catalysts prepared in situ from [$RuCl_2$(bmim)(η^6-*p*-cymene)] and the appropriate phosphine ligand. The reactions were run under argon at constant temperature either in Schlenk tubes (atmospheric pressure) or in home made thick-wall glass reactors (reactions under pressure). A representative example of the catalytic hydrodehalogenation of chloroform is as follows. 4.8 mg (0.01 mmol) of [$RuCl_2$(bmim)(η^6-*p*-cymene)] and 1.6 mg (0.01 mmol) pta was placed into a Schlenk tube closed by a rubber septum. The tube was evacuated then filled with argon gas several times. 1 mL of aqueous solution of HCOONa (136 mg, 2 mmol) was injected through the septum with needle, followed by 80 µL (1 mmol) of $CHCl_3$ containing 10 mg naphthalene (internal standard). The tube was immersed into a thermostated bath (80.0±0.1 °C) and the mixture was vigorously stirred for 120 min. After this time the reaction mixture was cooled to room temperature then kept in the freezer for 10 minutes. Then 1 mL of toluene (1 mL hexane in case of benzyl halides) was injected through the septum and the product mixture was thoroughly extracted at room temperature. The separated organic phase was filtered through a short column of anhydrous $\mathrm{MgSO_4}$ and analyzed by gas chromatography. Catalytic dehalogenation data disclosed in Tables and on Figures are means of 3-5 experiments.

2.3 *Synthesis of the [RuCl(bmim)(pta)(η^6-p-cymene)]Cl catalyst*

[RuCl(bmim)(pta)(η^6-*p*-cymene)]Cl was synthetized by reacting under argon 150 mg (0.34 mmol) [$\mathrm{RuCl_2}$(bmim)(η^6-*p*-cymene)] and 49.4 mg (0.34 mmol) pta in 10 mL dry methanol for 2 h at room temperature. The red reaction mixture was filtered through a HyfloSuperCell pad and evaporated to dryness to yield a sticky dark solid. This was triturated with several portions of diethyl ether after which an orange solid product was formed (164 mg, 81%). Elemental analysis (%): Found C, 46.27; H, 6.22; N, 10.66; Calculated for $\mathrm{C_{24}H_{40}N_5PCl_2Ru}$ C, 47.92; H, 6.70; N, 11.64. Despite all our efforts we were unable to obtain samples with elemental analysis closer to the calculated and the composition of the product was established mainly on basis of NMR and MS data.

Samples for ESI-MS were prepared in methanol and showed peaks corresponding to [RuCl(bmim)(pta)(η^6-*p*-cymene)]Cl at m/z 566.174 ($[\mathrm{M\text{-}Cl}]^+$, calc. 566.175) and 409.095 ($[\mathrm{M\text{-}Cl\text{-}pta}]^+$, calc. 409.098) with correct isotopic distribution patterns.

Characterization by ^{1}H, ^{13}C, and ^{31}P NMR-spectroscopy: ^{1}H NMR (400 MHz, 298 K, DMSO-$\mathrm{d_6}$) δ/ppm: 0.84 (t, 3H, $\mathrm{N\text{-}CH_2CH_2CH_2C}H_3$), 1.05 (d, 6H, $\mathrm{C}H_3\mathrm{\text{-}CH\text{-}C}H_3$), 1.19 (sextet, 2H, $\mathrm{N\text{-}CH_2CH_2C}H_2\mathrm{CH_3}$), 1.68 (quintet, 2H, $\mathrm{N\text{-}CH_2C}H_2\mathrm{CH_2CH_3}$), 1.83 (s, 3H, $\mathrm{C\text{-}C}H_3$), 2.45 (heptet, 1H, $\mathrm{CH_3\text{-}C}H\mathrm{\text{-}CH_3}$), 3.71 (s, 3H, $\mathrm{N\text{-}C}H_3$), 4.02 (t, 2H, $\mathrm{N\text{-}C}H_2\mathrm{CH_2CH_2CH_3}$), 4.12 (s, 6H, $\mathrm{PC}H_2\mathrm{N}$), 4.37 (s, 6H, $\mathrm{NC}H_2\mathrm{N}$), 5.67-5.70 (m, 4H, $\mathrm{\text{-}C}H\mathrm{\text{-}}$), 7.36 (d, 1H, $\mathrm{N\text{-}C}H\mathrm{{=}CH\text{-}N}$), 7.42 (d, 1H, $\mathrm{N\text{-}CH{=}C}H\mathrm{\text{-}N}$). ^{13}C NMR (100 MHz, 298 K, DMSO-$\mathrm{d_6}$) δ/ppm: 13.93 ($\mathrm{\text{-}CH_2}C\mathrm{H_3}$), 18.33 ($\mathrm{C\text{-}}C\mathrm{H_3}$), 19.51 ($\mathrm{N\text{-}CH_2CH_2}C\mathrm{H_2}$), 22.19 ($\mathrm{CH\text{-}}C\mathrm{H_3}$), 30.56 ($C\mathrm{H\text{-}CH_3}$), 33.43 ($\mathrm{N\text{-}CH_2}C\mathrm{H_2}$), 38.59 ($\mathrm{N\text{-}}C\mathrm{H_3}$), 50.97 ($\mathrm{N\text{-}}C\mathrm{H_2}$), 52.03 (d, $^1J_{\mathrm{P\text{-}C}}$= 16 Hz, $\mathrm{P}C\mathrm{H_2N}$), 72.66 (d, $^3J_{\mathrm{P\text{-}C}}$= 6 Hz, $\mathrm{N}C\mathrm{H_2N}$) 85.16, 88.37 ($C\mathrm{H\text{-}}C\mathrm{H}$), 95.44 ($C\mathrm{\text{-}CH_3}$), 104.48 ($C\mathrm{H\text{-}CH(CH_3)_2}$), 122.16,

123.36 (N-*C*H=*C*H-N), 178.51 (N*C*N). $^{31}P\{^{1}H\}$ NMR (162 MHz, 298 K, DMSO-d$_6$) δ/ppm: -35.54, -37.55, -38.50. Addition of [RuCl$_2$(pta)(η^6-*p*-cymene)] increased the intensity of the resonance at -35.54 ppm what shows that during the synthesis part of the bmim ligand in [RuCl$_2$(bmim)(η^6-*p*-cymene)] was replaced by pta.

After column chromatography on silica gel (eluent methanol:triethylamine=1:1) a brown sticky solid was obtained. This product showed two singlets in the ^{31}P NMR spectrum (solvent: 0.1 M KCl in D$_2$O, 298 K) at δ= -36.21 ppm and -36.93 ppm (in a 8/2 intensity ratio) the product mixture.

In contrast to the isolated product, mixing of aqueous solutions of [RuCl$_2$(bmim)(η^6-*p*-cymene)] and pta followed with heating for 30 min at 60°C yielded a solution displaying two singlet resonances in the ^{31}P NMR spectrum at -36.93 ppm and -37.53 ppm (in H$_2$O) with a 8/2 intensity ratio, and the reaction mixture contained only 4% of [RuCl$_2$(pta)(η^6-*p*-cymene)] impurity. This led us to investigate catalytic hydrodehalogenation of organic halides with catalysts prepared in situ from [RuCl$_2$(bmim)(η^6-*p*-cymene)] and the appropriate tertiary phosphine ligands.

3. Results and discussion

3.1 Dehalogenation of organic halides

[RuCl$_2$(bmim)(η^6-*p*-cymene)], **1** (Scheme 2) was found to efficiently catalyze hydrodehalogenation of aliphatic and aromatic halides. As yet, no similar half-sandwich Ru(II)-NHC complexes have been applied for catalytic hydrogenolysis of C-X (X = halogen) bonds in water.

In aqueous systems, **1** is known to dissociate chloride to yield [RuCl(H$_2$O)(bmim)(η^6-*p*-cymene)]$^+$ in which the aqua ligand can be easily displaced by phosphines [40]. The various [RuCl(bmim)(L)(η^6-*p*-cymene)] complexes formed in situ in the reaction of **1** with

L = *m*tppms, *m*tppts, pta, pta-Me or pta-Bn were also active in catalysis of hydrodehalogenation of various halides (Scheme 2). Data for dehalogenation of chloroform are given in Table 1.

As shown by the data in Table 1, **1** itself is an active catalyst of chloroform dehalogenation in the biphasic $CHCl_3/H_2O$ mixtures leading to 17.2% conversion in 2 hr. The catalytic activity can be increased by addition of pta or *m*tppms; in fact the highest conversion (25.8% in 2 h) was achieved with the latter ligand. Monosulphonated triphenylphosphine (*m*tppms) is a known surfactant [37] and this may facilitate the mass transport between the catalyst-containing aqueous phase and the organic phase of the neat substrate. The charged [RuCl(bmim)(*m*tppts)(η^6-*p*-cymene)]$^{2-}$, [RuCl(bmim)(pta)(η^6-*p*-cymene)]$^+$ and [RuCl(bmim)(L)(η^6-*p*-cymene)]$^{2+}$ complexes (L = pta-Bn or pta-Me) showed lower catalytic activity than [RuCl(bmim)(*m*tppms)(η^6-*p*-cymene)]. In general, the catalytic activities of the complexes in Table 1 compare favorably to literature data for homogeneous Ru(II) catalysts. For example, with $[RuCl_2(PPh_3)_3]$ catalyst Xie et al [18] observed 19 turnovers in 36 h (TOF = 0.53 h^{-1}) in hydrodehalogenation of $CHCl_3$ in xylene, while in the dehalogenation of benzyl chloride, Marčec et al [20] obtained a TOF=4.4 h^{-1} using HCOOLi as hydrogen source and refluxing dioxane as solvent. On the other hand, Bényei et al reported an outstandingly efficient system for hydrodehalogenation of CCl_4 and other aliphatic halides composed of [{$RuCl_2$(*m*tppms)$_2$}$_2$] + *m*tppms as catalyst and aqueous HCOONa as hydrogen donor. At 80°C, dehalogenation started with an initial TOF as high as 1000 h^{-1}, however, the reactions stopped abruptly at about 60% conversion of CCl_4 (although the average TOF for the total 3 hours reaction time was still a respectable 160 h^{-1}) [19].

In most of our further investigations on the details of catalytic hydrodehalogenation we used the catalyst prepared in situ from [RuCl$_2$(bmim)(η^6-*p*-cymene)] and pta. The effect of the [pta]/[Ru] ratio on the activity of the catalyst is shown on Figure 1. The highest activity was observed with a [pta]/[Ru] = 1/1 ratio, and this refers to the involvement of the known [RuCl(bmim)(pta)(η^6-*p*-cymene)]$^+$ mixed NHC-phosphine complex [40] among the most important catalytic species. Hydrodehalogenation of CHCl$_3$ was also carried out with the catalyst synthetized as described in the Experimental; essentially the same catalytic activity was observed (20.2% conversion in 2 h) as with corresponding in situ mixtures of **1** and pta (19.6 %, Table 1, Entry 3).

In the absence of HCOONa no reaction occured. However, with an increase of the formate concentration a steep increase of the reaction rate was observed followed by a plateau and even with a slight decrease; the highest conversion (21.6%) was determined at [HCOONa] = 2 M (Figure 2). The most probable explanation of the rate decrease above this formate concentration may be in the decreased solubility of CHCl$_3$ in such aqueous formate solutions. Nevertheless, the conversion could be increased with a simultaneous increase of both the formate concentration and the reaction time. Accordingly, CHCl$_3$ was dehalogenated with 36.4% conversion with 5 M HCOONa in 6 h (other conditions as in Figure 2).

On increasing the temperature the reaction rate increased exponentially. While hardly any conversion (1.2%) was detected at 40°C, 34.3% of the substrate CHCl$_3$ was converted to CH$_2$Cl$_2$ at 90°C in 2 h (Figure 3). Conversions in the first 2 h represent well the initial rates of CHCl$_3$ dehalogenations (Figure 4) and the data gave a good linear Arrhenius plot (R^2 =

0.999) allowing calculation of a formal activation energy of E_a=64.0 kJ/mol. Note that in addition to changes in the rate of the various steps of the chemical reaction with changing temperatures, in a liquid biphasic system the rate of the overall reaction may be influenced also by changes in the solubility of the substrate(s) and product(s) in the two liquid phases (themselves temperature dependent).

Table 2 summarizes the results of the hydrodehalogenation of various organic halides with the $[RuCl(bmim)(pta)(\eta^6\text{-}p\text{-cymene})]^+$ catalyst in aqueous formate solutions. In accord with the reactivity of $CHCl_3$, the reaction of carbon tetrachloride yielded both chloroform and dichloromethane (entries 1, 2). Concerning the reactivities of various substrates, our findings follow the expected trends. Accordingly, aliphatic halides reacted faster than halobenzenes, so much that in the case of bromo- and iodobenzene the reaction times had to be extended from 2 to 19 h to achieve meaningful conversions (chlorobenzene still gave low yield of benzene). The reactivity order was R-Cl < R-Br < R-I; these results are in agreement with the general reactivity of the C-Halogen bonds. Dehalogenation of benzyl halides was accompanied by hydrolysis to benzyl alcohol and for that reason it was not investigated in more detail.

While dehalogenation proceeded effectively under argon with HCOONa as the hydrogen source, H_2 alone proved insufficient, and formate, too, had to be given to initiate the reactions. In the presence of HCOONa, admisson of 10 bar H_2 caused noticeable changes in the conversions of the most reactive substrates (CCl_4 and $CHBr_3$, entries 2 and 6). Conversely, dehalogenation of $CHCl_3$ was only slightly influenced by H_2 and this effect was not further scrutinized.

Under the standard reaction conditions, hydrodehalogenation of $CHCl_3$ proceeded smoothly and no other product than CH_2Cl_2 was observed. However, the time course of the reaction (Figure 4) revealed that the reactions stopped well before 100% conversion of the substrate (31.0% conv. in 4 h). With the more reactive $CHBr_3$ (initial TOF = 112 h^{-1}) higher conversions were observed (86.5% conv. in 4 h), although there was no complete conversion in this case either.

or $CHCl_3$; 0.01 mmol [$RuCl_2$(bmim)(η^6-*p*-cymene)] (**1**); 0.01 mmol pta; 2.0 mmol HCOONa; solvent = 1 mL H_2O; T = 80°C; argon atmosphere (1 bar).

3.2 *Catalysis of formate dehydrogenation concomitant to hydrodehalogenation*

A possible explanation of incomplete conversions of organic halides is in the catalytic decomposition of formate to H_2 and HCO_3^- (Eq. 1) concomitant to dehalogenation. Formate decomposition is a reaction of great interest since –when coupled to catalytic hydrogenation of bicarbonate– it can serve as basis for reversible hydrogen storage/delivery systems. As yet only a few Ru(II)- and Ir(I)-based homogeneous catalysts have been identified capable for catalysis of the reversible reaction (1) in both directions, influenced only by the hydrogen pressure [42, 43, 51-53].

$$HCO_2^- + H_2O \rightleftharpoons H_2 + HCO_3^- \qquad (1)$$

Indeed, we have found that under the reaction conditions of dehalogenation but in the absence of an organic halide, [RuCl(bmim)(pta)(η^6-*p*-cymene)]$^+$ catalyzed the formation of H_2 from aqueous formate - the reaction could be followed by using an atmospheric gas burette. The results show (Figure 5) that 13% of the initial formate decomposed in 2 h at 80°C. This is in good agreement with the 77.6% dehalogenation of $CHBr_3$ during the same time (Figure 4). Note that dehalogenation of $CHBr_3$ stopped completely after 4 h (maximum conversion 86%), apparently due to lack of formate.

With the aim to assess the role of formate decomposition in hydrodehalogenation of haloorganics, we studied the kinetics of H_2 evolution. The initial rates of H_2 evolution at temperatures at which the reaction could be followed by gas volumetry were determined from the slopes of the linear parts of the graphs in the 15-40 min intervals (Figure 5). An Arrhenius-plot of these data yielded an activation energy of E_a = 119 kJ/mol. There are only a few data in the literature on the activation energy of catalytic decomposition of HCOONa in aqueous solution yielding H_2 and bicarbonate. The closest to our system is the dehydrogenation of aqueous Na-formate by the half-sandwich η^6-arene complex catalyst obtained in situ from [{$RuCl_2$(benzene)}$_2$] + 1,2-bis(diphenylphosphino)methane (dppm) studied by Beller and co-workers [52]. They reported initial rates of formate decomposition at 60°C and at 40°C (in DMF/H_2O solvent mixtures); from the data an activation energy of 83 kJ/mol can be calculated. This is significantly less than the value determined by us for [RuCl(bmim)(pta)(η^6-*p*-cymene)]$^+$ for formate dehydrogenation (119 kJ/mol) but still substantially higher than the apparent activation energy of hydrodehalogention of $CHCl_3$ by the same complex (64.0 kJ/mol, see *3.1*).

3.3 Reactions of [RuCl(bmim)(pta)(η^6-p-cymene)]$^+$ with aqueous $HCOO^-$

Addition of 1 equivalent of pta to a solution of [$RuCl_2$(bmim)(η^6-*p*-cymene)] in H_2O resulted in an immediate color change from orange to yellow. After heating the reaction mixture for 30 min at 60°C two singlet resonances were observed in the ^{31}P NMR spectrum at -36.93 and -37.53 ppm (in H_2O) in a 8/2 ratio. The main component in this solution is [RuCl(bmim)(pta)(η^6-*p*-cymene)]$^+$ (δ= -36.93 ppm) [40]. Since aquation of [$RuCl_2$(bmim)(η^6-*p*-cymene)] is known to yield [RuCl(H_2O)(bmim)(η^6-*p*-cymene)]$^+$ we assign the less intensive ^{31}P resonance at δ= -37.53 ppm to [Ru(H_2O)(bmim)(pta)(η^6-*p*-cymene)]$^{2+}$. Addition of 50 equivalents of HCOONa at room temperature caused a shift of these singlets to -36.99 ppm and -37.60 ppm. Upon heating this solution at 80°C for 30 min, ^{1}H-NMR showed two doublets in the hydride region centered at δ = -10.92 ppm ($^{2}J_{H\text{-}P}$=52.9 Hz) and at -10.95 ppm ($^{2}J_{H\text{-}P}$=52.9 Hz). Similarly, in the ^{31}P NMR spectrum two doublets were observed at δ = -21.55 ppm ($^{2}J_{P\text{-}H}$=51.5 Hz) and δ = -21.70 ppm ($^{2}J_{P\text{-}H}$=52.5 Hz). Proton decoupling led to collapse of these doublets to singlets, similarly, the doublets in the hydride region collapsed to singlets upon phosphorus decoupling. These spectral data are consistent with the presence of half-sandwich monohydrido complexes [RuH(bmim)(pta)(η^{6}-*p*-cymene)]$^{+}$ (major product, ^{31}P{^{1}H} δ = -21.55 ppm, ^{1}H{^{31}P} δ = -10.95 ppm) and probably [RuH(HCOO)(pta)(η^{6}-*p*-cymene)] (minor product, ^{31}P{^{1}H} δ = -21.70 ppm, ^{1}H{^{31}P} δ = -10.92 ppm). Presence of [RuHX(pta)(η^{6}-*p*-cymene)]$^{n+}$ (X=Cl^{-}, n=0; X=H_2O, n=1) complexes can be excluded since they show doublets in the ^{1}H NMR spectra at δ = -10.35 and -10.43 ppm (singlets in ^{1}H{^{31}P} NMR, in both cases $^{2}J_{P\text{-}H}$ = 40 Hz) [54]. Under no conditions were triplet hydride resonances observed in the ^{1}H NMR spectra, so despite the lability of the complexes and possible redistribution of pta among various ruthenium species (as observed in case of similar Ru(II)-arene-pta complexes [54]) formation of hydrido-bisphosphine-Ru(II) species (such as e.g. [RuH(pta)$_2$(η^{6}-*p*-cymene)]$^{+}$ [54]) during catalysis need not be considered.

3.4 Suggested reaction mechanism of simultaneous hydrodehalogenation and formate dehydrogenation catalyzed by [RuCl(bmim)(pta)(η⁶-p-cymene)]⁺

On the basis of the kinetic and structural findings described in *3.1-3.3*, the following mechanism is suggested for the simultaneous hydrodehalogenation and formate dehydrogenation (Scheme 3).

As shown on Scheme 3, in a fast reaction [RuCl$_2$(bmim)(η^{6}-*p*-cymene)] and pta yield [RuCl(bmim)(pta)(η^{6}-*p*-cymene)]$^{+}$ in which chloride is replaced easily by formate. Heating the aqueous solution to 80°C induces decomposition of coordinated $HCOO^-$ with release of CO_2 (as HCO_3^-) and concomitant formation of [RuH(bmim)(pta)(η^6-*p*-cymene)]$^+$. The hydride ligand of this complex attacks the positively polarized carbon in the substrate (e.g. $CHCl_3$) which also results in the split of the C-Cl bond to yield the dehalogenated product (CH_2Cl_2). The resulting coordinatively unsaturated Ru(II)-moiety may pick up a chloride or formate and enters again the catalytic cycle of hydrodehalogenation. Alternatively, [RuH(bmim)(pta)(η^6-*p*-cymene)]$^+$ is protonated to yield H_2 and in the presence of excess $HCOO^-$ provides [Ru(HCOO)(bmim)(pta)(η^6-*p*-cymene)]$^+$ (hydrogen generation cycle). With this catalyst, formate decomposition (E_a = 119 kJ/mol) cannot be rate determining in hydrodehalogenation of $CHCl_3$ for which an activation energy of 64.0 kJ/mol was determined. Obviously, the two activation energy values belong to different steps in the relevant catalytic cycles. It seems reasonable to assume that in hydrodehalogenation the hydride transfer from the metal to carbon in the $C^{\delta+}$-$Cl^{\delta-}$ bond is the rate determining step, while in case of formate dehydrogenation it is the release of H_2 from the [RuH(bmim)(pta)(η^6-*p*-cymene)]$^+$ intermediate which limits the rate of H_2 generation.

Summary

In summary, we have succesfully used for the first time water-soluble mixed-ligand Ru(II)-NHC-phosphine complex catalysts such as [RuCl(bmim)(pta)(η^6-*p*-cymene)]$^+$ for hydrodehalogenation of organic halides by hydrogen transfer from sodium formate in aqueous media with turnover frequencies up to TOF=112 h^{-1} at 80°C. The reactions proceed in purely aqueous media and require no organic solvents, bases or other additives. [$RuCl_2$(bmim)(η^6-*p*-cymene)] (**1**) and the water-soluble [RuCl(bmim)(L)(η^6-*p*-cymene)] complexes (L=*m*tppms, *m*tppts, pta-Me and pta-Bn) derived from **1** in reaction with L were also active in hydrodehalogenation but –except the *m*tppms derivative– showed lower activity than [RuCl(bmim)(pta)(η^6-*p*-cymene)]$^+$. Aliphatic as well as aromatic halides could equally be dehalogenated with decreasing reactivity in this order. It was also found that in addition to hydrodehalogenation [RuCl(bmim)(pta)(η^6-*p*-cymene)]$^+$ catalyzed also the decomposition of aqueous formate to H_2 and bicarbonate. Kinetics of both hydrodehalogenation and formate decomposition were studied and a possible reaction mechanism was suggested involving [RuH(bmim)(pta)(η^6-*p*-cymene)]$^+$ as the key catalytic species in both reactions.

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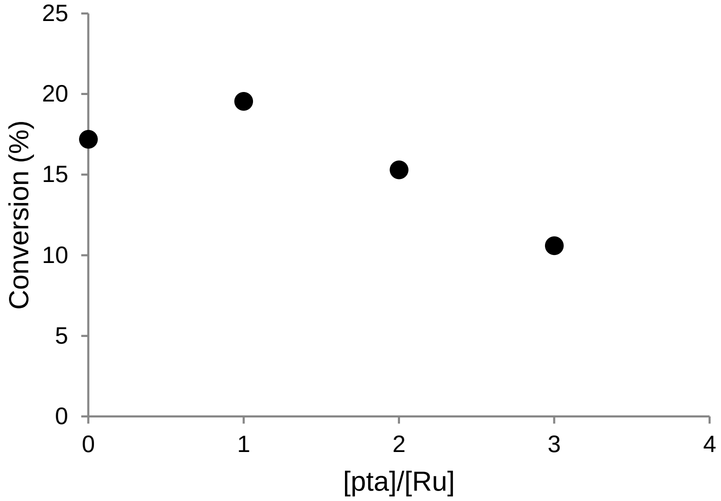


Figure 1. Hydrodehalogenation of $CHCl_3$ by aqueous Na-formate; effect of the [pta]/[Ru] ratio on the activity of the catalyst formed in situ from [$RuCl_2$(bmim)(η^6-*p*-cymene)] and pta. *Conditions:* 1.0 mmol $CHCl_3$; 2.0 mmol HCOONa; 0.01 mmol [$RuCl_2$(bmim)(η^6-*p*-cymene)] (**1**); solvent = 1 mL H_2O; argon atmosphere (1 bar); *T* = 80°C; *t* = 2 h.

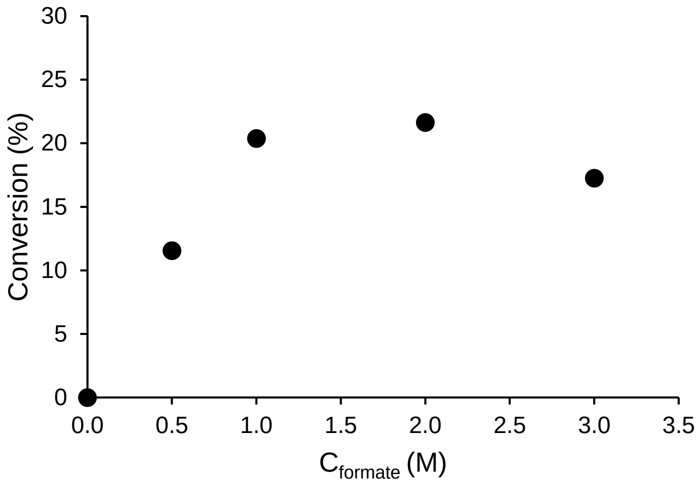


Figure 2. Hydrodehalogenation of $CHCl_3$ with aqueous Na-formate catalyzed by [$RuCl_2$(bmim)(η^6-*p*-cymene)] + pta; conversion as a function of formate concentration. *Conditions:* 1.0 mmol $CHCl_3$; 0.01 mmol [$RuCl_2$(bmim)(η^6-*p*-cymene)] (**1**); 0.01 mmol pta; solvent = 1 mL H_2O; argon atmosphere (1 bar); *T* = 80°C; *t* = 2 h.

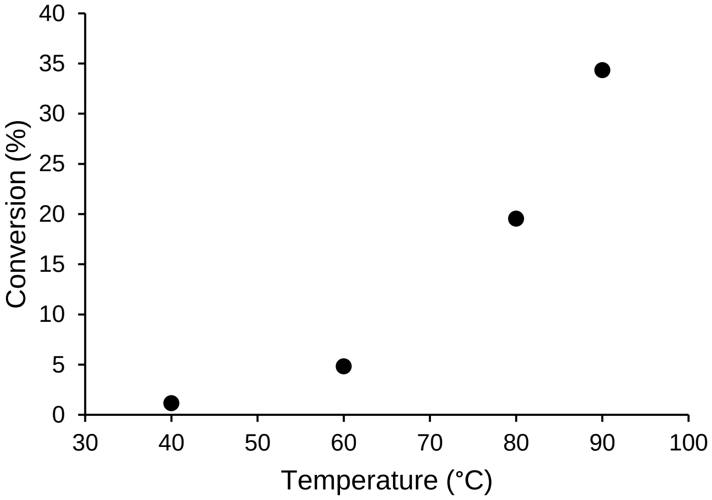


Figure 3. Hydrodehalogenation of $CHCl_3$ with aqueous Na-formate catalyzed by $[RuCl_2(bmim)(\eta^6\text{-}p\text{-cymene})]$ + pta; conversion as a function of the temperature. *Conditions:* 1.0 mmol $CHCl_3$; 0.01 mmol $[RuCl_2(bmim)(\eta^6\text{-}p\text{-cymene})]$ (**1**); 0.01 mmol pta; 2.0 mmol HCOONa; solvent = 1 mL H_2O; argon atmosphere (1 bar); $t = 2$ h.

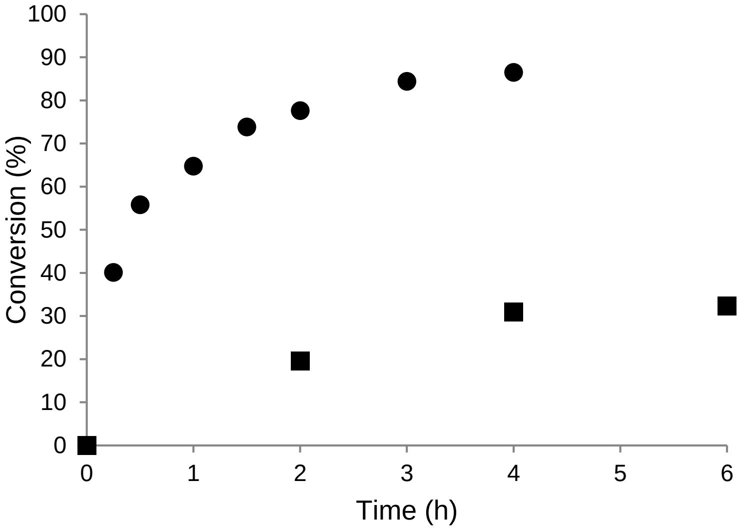


Figure 4. Time course of the hydrodehalogenation of $CHBr_3$ (●) and $CHCl_3$ (■) with aqueous Na-formate catalyzed by [$RuCl_2$(bmim)(η^6-*p*-cymene)] + pta. *Conditions:* 1.0 mmol $CHBr_3$

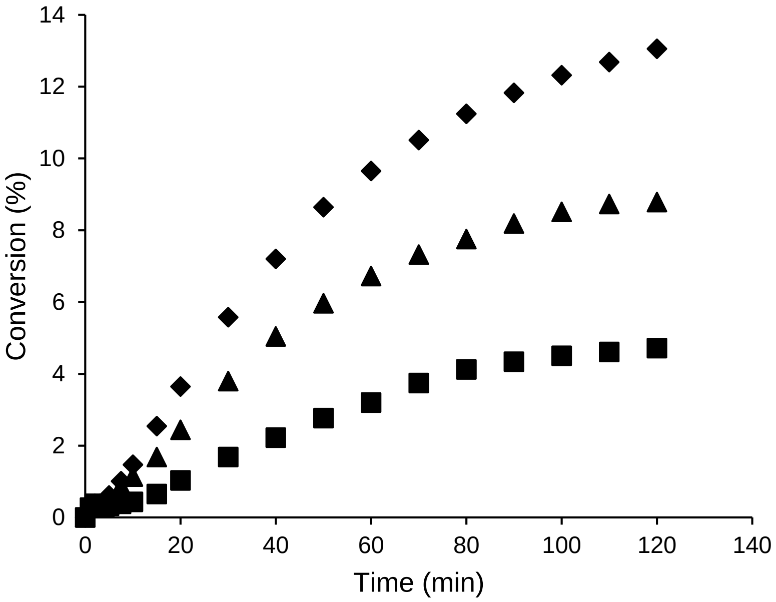
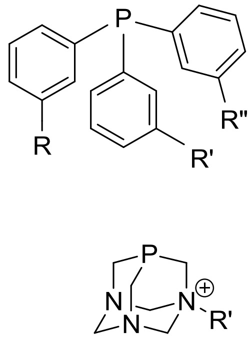


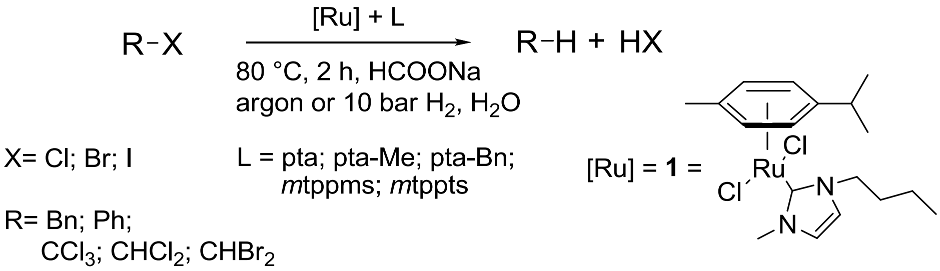
Figure 5. Time-course of H_2 evolution in decomposition of aqueous HCO_2^- catalyzed by $[RuCl_2(bmim)(\eta^6$-*p*-cymene)] + pta at various temperatures. *Conditions:* 0.01 mmol $[RuCl_2(bmim)(\eta^6$-*p*-cymene)] (**1**); 0.01 mmol pta; 2.0 mmol HCOONa; solvent = 1 mL H_2O; *T* = 70°C (■), 75°C (▲) and 80°C (♦) ; initial atmosphere: argon (1 bar).



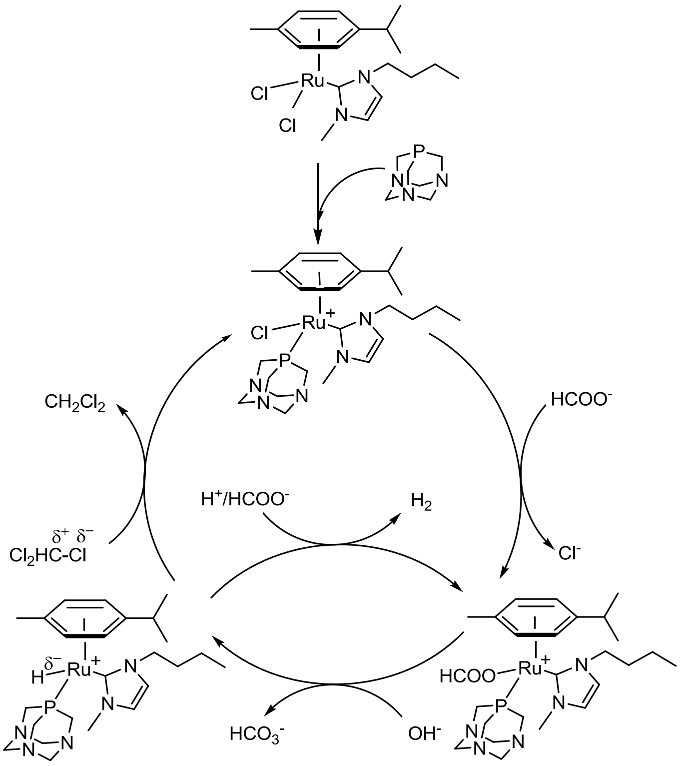
*m*tppts: R=R'=R''= SO_3^-
*m*tppms: R= SO_3^-, R'=R''=H

pta: R'= -
pta-Me: R'= $-CH_3$
pta-Bn: R'= $-CH_2C_6H_5$

Scheme 1. Water-soluble phosphines used in this study



Scheme 2. General scheme of hydrodehalogenation of organic halides



Scheme 3. Suggested mechanism of hydrodehalogenation of organic halides and concomitant dehydrogenation of aqueous formate catalyzed by the [RuCl$_2$(bmim)(η^6-*p*-cymene)] + pta catalyst

Table 1. Hydrodehalogenation of $CHCl_3$ with aqueous Na-formate catalyzed by **1** and by the [RuCl(bmim)(L)(η^6-*p*-cymene)] complexes formed in situ in the reaction of **1** with L.

Entry	L	Conversion (%)	TOF (h^{-1})
1[a, b]	pta	0	0
2	-	17.2	8.5
3[a]	pta	19.6	9.8
4[a]	pta-Bn	13.9	6.9
5	pta-Me	7.6	3.8
6	*m*tppms	25.8	12.9
7	*m*tppts	11.7	5.8

Conditions: 1.0 mmol $CHCl_3$; 2.0 mmol HCOONa; 0.01 mmol [$RuCl_2$(bmim)(η^6-*p*-cymene)] (**1**); 0.01 mmol L; solvent = 1 mL H_2O; $P(H_2)$ = 10 bar; T = 80°C; t = 2 h; [a] argon atmosphere (1 bar); [b] without **1.**

Table 2. Hydrodehalogenation of organic halides with aqueous Na-formate catalyzed by the mixed-ligand NHC-phosphine complex formed in situ from [$RuCl_2$(bmim)(η^6-*p*-cymene)] and pta.

Entry	Substrate	Time (h)	Atmosphere	Conversion (%)	Products (%)
1	CCl_4	2	Ar	29.7	$CHCl_3$ (18.0) + CH_2Cl_2 (11.7)
2	CCl_4	2	H_2	41.9	$CHCl_3$ (29.0) + CH_2Cl_2 (12.9)
3	$CHCl_3$	2	Ar	19.6	CH_2Cl_2
4	$CHCl_3$	2	H_2	21.6	CH_2Cl_2
5	$CHBr_3$	2	Ar	77.6	CH_2Br_2
6	$CHBr_3$	2	H_2	66.4	CH_2Br_2
7	PhBr	2	Ar	0.7	Benzene
8	PhCl	19	Ar	1.7	Benzene
9	PhBr	19	Ar	7.4	Benzene
10	PhI	19	Ar	26.5	Benzene

Conditions: 1.0 mmol substrate; 2.0 mmol HCOONa; 0.01 mmol [$RuCl_2$(bmim)(η^6-*p*-cymene)] (**1**); 0.01 mmol pta; solvent = 1 mL H_2O; $T = 80°C$; $P(Ar) = 1$ bar; $P(H_2) = 10$ bar.