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Review

Synthesis and catalytic applications of Ru(II)-phosphaurotropine complexes with the use of simple water-soluble Ru(II)-precursors ☆

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ABSTRACT

1,3,5-Triaza-7-phosphaadamantane (pta, phosphaurotropine) played a special role in the development of aqueous organometallic chemistry and catalysis. The main reason is in its easy synthesis, oxidation stability, versatile possibilities of functionalization, and high solubility not only in water but also in several common organic solvents. Such favourable solubility behaviour allowed straightforward synthesis of pta-containing transition metal complexes from simple, inexpensive, often commercial starting materials. A further advantage of pta and its complexes is in their pronounced tendency to crystallize which allowed determination of solid-state structures of a great number of such compounds. This review covers synthetic procedures of ruthenium(II)-complexes with pta, and *N*-alkyl-pta derivatives as ligands, as well as their most important reactions in aqueous systems. Ru(II)-pta complexes were employed as catalysts in several important aqueous-phase processes such as selective hydrogenation and transfer hydrogenation of aldehydes, hydration of nitriles, and redox isomerization of allylic alcohols. Hydrogenation of carbon dioxide/bicarbonate and dehydrogenation of formic acid/aqueous formate were also studied with various Ru(II)-complexes of phosphaurotropines. Altogether the results described in this review made a significant positive impact on the development of green chemical processes.

Contents

Abbreviations: [9]aneS$_3$, 1,4,7-trithiacyclononane; bipy, 2,2′-bipyridine; cinnamaldehyde, 3-phenyl-2-propenal; cinnamyl alcohol, 3-phenyl-2-propenol; Cp*, $C_5(CH_3)_5^-$, η^5-pentamethylcyclopentadienyl; Cp', a general η^5-cyclopentadienyl ligand; Cp, $C_5H_5^-$, η^5-cyclopentadienyl; dapta, 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane; dmso, dimethylsulfoxide; Dp, η^5-1,2-dihydropentalenyl; ESI-MS, electrospray ionization mass spectrometry; FA, formic acid; Ind, η^5-indenyl; MeCN, acetonitrile; MR, Merrifield resin; *m*tppms-Na, sodium 3-diphenylphosphinobenzenesulfonate (monosulfonated triphenylphosphine); *m*tppts-Na$_3$, trisodium 3,3′,3′′-phosphinetriylbenzene sulfonate (trisulfonated triphenylphosphine); nano-RAPTA, RAPTA immobilized on silica-coated Fe_3O_4 nanoparticles; NHC, N-heterocyclic carbene; OTf, trifluoromethanesulfonate; *p*-cymene, *p*-isopropyltoluene; PPh_3, triphenylphosphine; pta, 1,3,5-triaza-7-phosphaadamantane, 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane; pta-Bn, N-benzyl-pta; pta-Me, N-methyl-pta; pta-MR, Merrifield resin-immobilized pta; RAPTA, a Ru-arene-pta complex, or specifically [(η^6-*p*-cymene)$RuCl_2$(pta)]; salicylaldehyde, 2-OH-benzaldehyde; SC-XRD, single crystal X-ray diffraction; TOF, turnover frequency, TON×(time)$^{-1}$; TON, (mol reacted substrate)×(mol catalyst)$^{-1}$; tos, *p*-toluenesulfonate; α-terpinene, 1-isopropyl-4-methyl-1,3-cyclohexadiene.

☆ Dedicated to Professor Maurizio Peruzzini in recognition of his numerous outstanding achievements in inorganic, coordination, structural, and biochemistry, and his tremendous contributions to the advancement of international scientific cooperation.

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1. Introduction

Sustainable development requires chemical processes which – in contrast to those presently in use– do not damage the environment. Most of the chemical reactions take place in volatile, inflammable, explosive, toxic and often very expensive solvents the use of which should be minimized in chemical processes. Chemistry in living organisms takes place in aqueous conditions, and this solution of Nature may give an example to follow. Water is an ideal solvent, since it is an environment-friendly, colour- and odourless, non-flammable fluid, furthermore, it is cheap and abundant, too. In evaluations of health, safety and environmental effects, water consistently ranked among the most preferred (recommended) solvents, despite that its purification is excessively expensive; this may result in the choice of other, similarly green solvents for a particular technology. From the point of view of aqueous-organic biphasic catalysis, it is a further advantageous feature of water that it has only limited miscibility with a good many of organic solvents. This gives an excellent possibility to separate and reuse a water-soluble catalyst from organic-soluble substrates and products, not only making the actual chemical process greener but allowing an economical application of the often pricey soluble (homogeneous) catalysts [1–9].

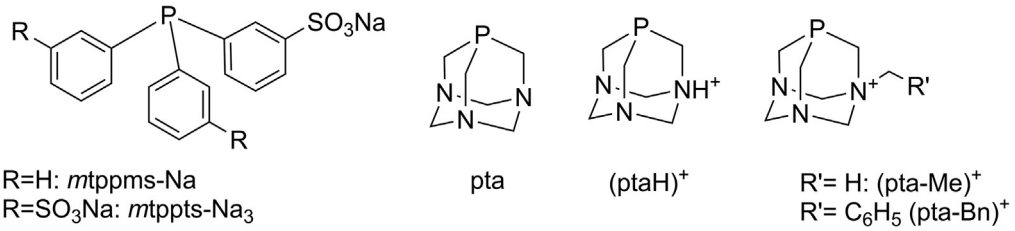
In the early 1970-ies, for hydrogenations in aqueous solutions, water-soluble variants of [$RuCl_2(PPh_3)_3$] and [$RhCl(PPh_3)_3$] were introduced as catalysts [10–11], in which the PPh_3 ligand was replaced by its monosulfonated derivative, diphenylphosphinobenzene-*m*-sulfonic acid, Na salt (*m*tppms-Na) [12]. The Rh(I)-complex with *m*tppts-Na_3 ligand (Scheme 1) is used in the aqueous biphasic hydroformylation of propene on an industrial scale (Ruhrchemie-Rhône Poulenc process) [13].

The most frequently followed procedure of obtaining water-soluble transition metal catalysts is the introduction of ionic or highly polar groups into ligands of efficient water-insoluble catalysts. However, neutral phosphine ligands which dissolve both in water and in organic solvents may be most useful in synthesis of metal complex catalysts and in studies on solvent effects in catalytic reactions.

By replacing one nitrogen atom in urotropine (hexamethylenetetramine) with phosphorus, a similar caged compound, 1,3,5-triaza-7-phosphaadamantane (pta; 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane) is obtained, which has high solubility both in water ($S_{(H2O),25°C}$ = 235 g/L ; 1.5 M [17]) and in several polar organic solvents [14–17]. On the basis of its basicity and structural parameters (P-C bonds and angles, as well as its overall size) it can be viewed as a water-soluble variant of trimethylphosphine (PMe_3). However, in contrast to most aliphatic phosphines, pta is stable against oxidation and can be handled in air. Several of its properties resemble those of urotropine rather than those of a tertiary phosphine. For example, in dilute acids pta is protonated on one of its three N-atoms instead of the phosphorus [16] and with alkyl halides it yields ammonium salts, instead of phosphonium derivatives [14–15].

This paper deals with complexes of only those pta derivatives which are shown on Scheme 1. Nevertheless, research on pta has led to synthesis and study of a large number of other pta derivates, too, which are described in excellent reviews [17–20]. It is also clear from these reviews, that pta coordinates with its N-donor atom(s) only to a relatively few metal ions, such as Mn(II), Zn(II), Cd(II), and that in its complexes with platinum metal group ions pta is almost exclusively P-coordinated [17–20].

The report on the first synthesis of pta by Daigle in 1974 [14] was soon followed by two seminal papers by M.Y. Darensbourg et al on complexes of tungsten and molybdenum [21,22]. Apart from these investigations, coordination properties of pta were hardly studied; even the few reported investigations used strictly anhydrous solvents [21–23]. The first Ru(II)- and Rh(I)- complexes were described in 1992 by D.J. Darensbourg, Joó, Kathó et al [24]. Although since then, a high number of pta complexes with various metal ions have been prepared, complexes with Ru(II) as the cen-



Scheme 1. Sulfonated triphenylphosphines, pta and its derivatives.

tral metal ion retained their utmost popularity, due not only to their versatile catalytic applications but also to their beneficial physiological properties [17–20].

In this review, we describe the synthesis and catalytic applications of the first Ru(II)-pta complexes [24–25] and present the most notable developments of the last nearly 30 years in these fields. Emphasis is put on the special effects of pta and its derivatives on catalysis.

Several Ru-based complexes were obtained in ethanol or water as the solvent in the reaction of pta (or N-methyl pta) with hydrated RuX_3 (X = Cl or Br). We have conceived that water-soluble, substitutionally labile Ru(II)-complexes with precisely known composition, such as *cis*-$[RuCl_2(dmso)_4]$ [26–27] or $[Ru(H_2O)_6](tos)_2$ (tos = *p*-toluenesulfonate) [28] could be used beneficially for the syntheses. Indeed, we succeeded in preparing the first Ru(II)-pta complexes obtained from these precursors. In a similar approach, it was disclosed in the literature, that the water-soluble $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ (arene: *p*-cymene = *p*-isopropyltoluene; benzene) complexes [29–30], available commercially or easily obtained from hydrated Ru(III)-chloride were useful starting materials for synthesis of Ru(II)-pta complexes. Description of synthetic methods constitutes the first part of this paper.

The complexes obtained by in situ aqueous synthesis show similar (sometimes greater) efficiency in aqueous-organic biphasic catalysis than the same compounds prepared in organic solvents. Often, however, formation of various metal complexes may take place under aqueous conditions, and the number and composition of those may depend on the [ligand]/[Ru] ratio. Conversely, it is advantageous, that the coordination sphere of the Ru(II)-ion, hence the catalytic properties of the formed complex can be modified easily by addition of auxiliary (usually ionic) compounds. It should be always remembered, though, that even the ions of (so-believed) innocent buffer substances may coordinate, as well as H_2O itself (or OH^-, depending on the pH). Specific effects of the aqueous media, too, are treated in this review, with special emphasis on the influence of the aqueous environment on the chemoselectivity of certain catalytic reactions.

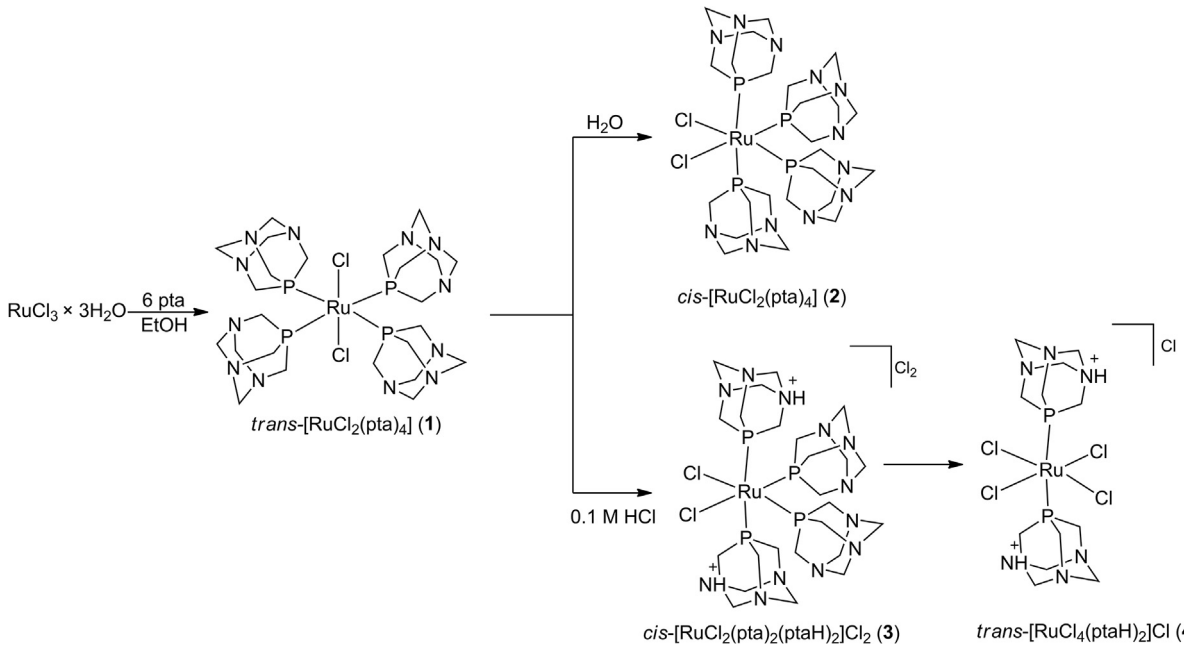
Efforts were made to compare the catalytic properties of Ru(II)-pta complexes to those of similarly water-soluble Ru(II)-complex catalysts which contain aromatic phosphine ligands. Perhaps the best known compound of the latter group is $[\{RuCl(m\text{tppms-}Na)_2\}_2(\mu\text{-}Cl)_2]$, a catalyst for several reactions, such as, for example, the hydrogenation of aldehydes, redox isomerization of allylic alcohols and hydrogenation of bicarbonate, HCO_3^-. These reactions are also catalyzed by $[RuCl_2(pta)_4]$, and by a few further Ru(II)-complexes which may be obtained in situ with the use of *cis*-$[RuCl_2(dmso)_4]$, or $[\{(\eta^6\text{-arene})RuCl_2\}_2]$ (arene: *p*-cymene; benzene) precursors. Interestingly, the hydration of nitriles is not catalyzed by $[\{RuCl(m\text{tppms-}Na)_2\}_2(\mu\text{-}Cl)_2]$, in contrast, it is effectively facilitated by Ru(II)-pta complexes; this reaction is also discussed.

2. Synthesis of Ru(II)-complexes containing phosphaurotropine ligands from water-soluble Ru(II)-precursors

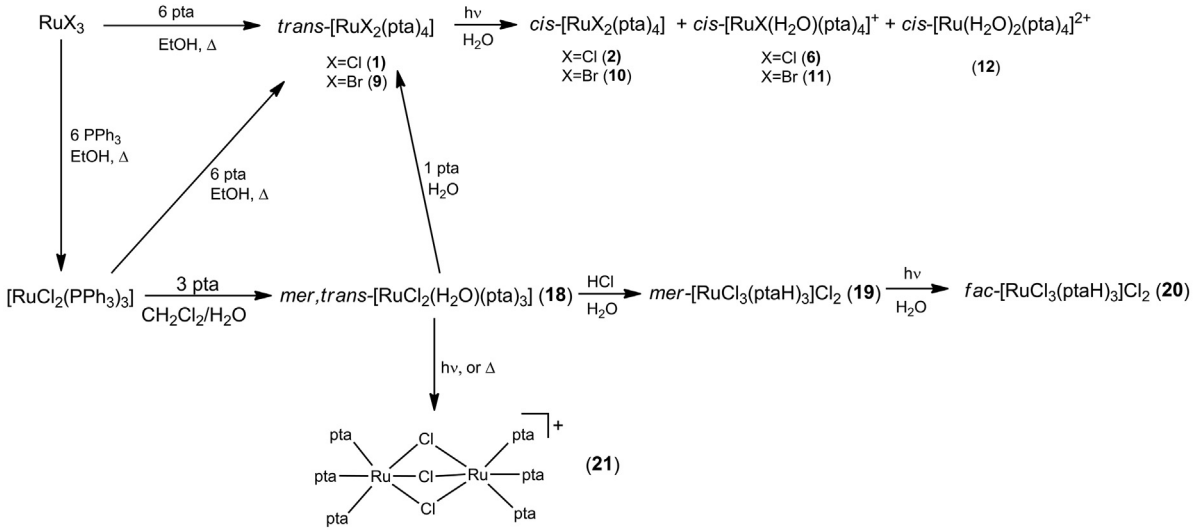
2.1. Synthesis of Ru(II)-complexes containing pta or its derivatives from hydrated Ru(III) halides

The first synthesis of Ru(II)-pta complexes followed the method for the synthesis of $[\{RuCl(m\text{tppms-}Na)_2\}_2(\mu\text{-}Cl)_2]$ [10–11]. Accordingly, a solution of hydrated $RuCl_3$ with 6 equivalents of pta was refluxed in 96% ethanol yielding a yellow precipitate. The ^{31}P NMR spectrum of this precipitate showed only one resonance at δ = –47.3 ppm (s) revealing the equivalency of coordinated phosphorus atoms. This NMR feature could be assigned to *trans*-$[RuCl_2(pta)_4]$ (**1**), however, upon recrystallization of the yellow precipitate from water, the thermodynamically more stable *cis*-$[RuCl_2(pta)_4]$ (**2**) was obtained. Recrystallization from 0.1 M HCl yielded yellow crystals, but after several weeks, a few black crystals appeared, too. Single crystal X-ray diffraction (SC-XRD) measurements established the composition of these compounds as *cis*-$[RuCl_2(pta)_2(ptaH)_2]Cl_2{\cdot}4H_2O$ (**3**·$4H_2O$; yellow), and *trans*-$[RuCl_4(ptaH)_2]Cl{\cdot}4H_2O$ (**4**·$4H_2O$; black) [24–25]. Scheme 2 shows the formation of **1**–**4**.

Peruzzini and co-workers also prepared **2** as yellow powder, furthermore, upon its recrystallization from water, they have obtained black crystals of the neutral *trans*-$[RuCl_4(ptaH)_2]{\cdot}4H_2O$ (**5**·$4H_2O$), too [31]. It is probable that oxidation of **5** leads to **4**,



Scheme 2. Formation of $[RuCl_2(pta)_4]$ and its protonated derivatives [24–25].



Scheme 3. Synthesis of mono- and dinuclear Ru(II)-pta complexes from hydrated RuX_3 (X = Cl or Br).

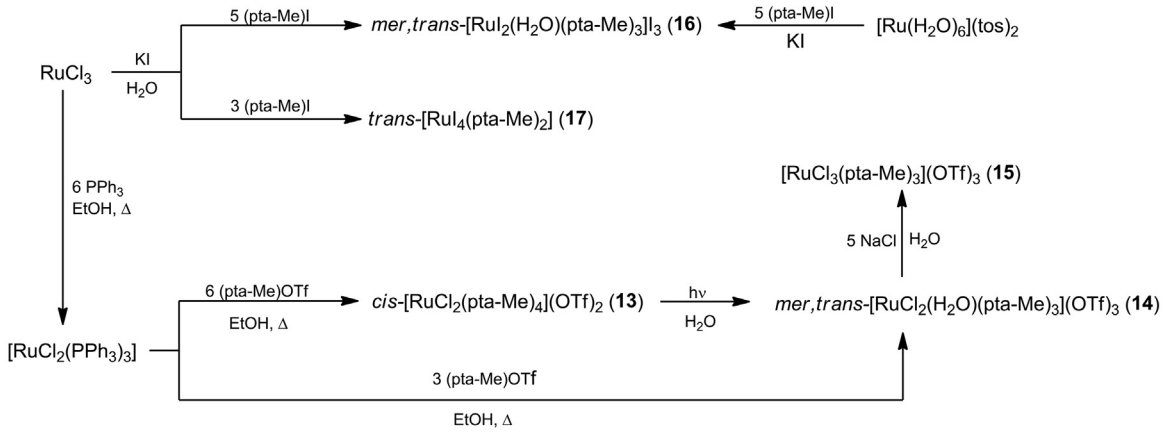
which was prepared a few years ago with almost quantitative yield in the reaction of pta and *trans*-$[RuCl_4(dmso)_2]^{2-}$ [32].

Frost and co-workers succeeded in crystallization of *trans*-$[RuCl_2(pta)_4]$ (**1**) from dichloromethane. In $CDCl_3$ solution, the intensity of the ^{31}P NMR signal of this product decreased in time and simultaneously resonances of *cis*-$[RuCl_2(pta)_4]$ (**2**) grew in. A steady intensity ratio of the signals, i.e. the equilibrium state was reached in 7 days. In contrast, during the same time in D_2O, the signal of *trans*-$[RuCl_2(pta)_4]$ disappeared completely, and only the resonances of *cis*-$[RuCl_2(pta)_4]$, and those of a presumably $[RuCl_n(H_2O)_{6-n}(pta)_4]$ species were observed [33].

Romerosa and co-workers have found that when dissolved in $CDCl_3$ in the dark, *trans*-$[RuCl_2(pta)_4]$ was not transformed into the corresponding *cis*-isomer, however, upon irradiation with visible light ($\lambda > 416$ nm) isomerization took place with 100% conversion. Based on the changes of the uv–vis spectra of the solutions, it was also found that this isomerization was fully reversible on the effect of irradiation with light of $\lambda = 367$ nm wavelength: after 20 min exposure of a 0.1 M *cis*-$[RuCl_2(pta)_4]$ solution, only the spectrum of **1** was detectable. This reversibility was not observed in aqueous solutions, instead, irradiation of an aqueous solution of *trans*-$[RuCl_2(pta)_4]$ (**1**) at $\lambda > 416$ nm yielded *cis*-$[RuCl(H_2O)(pta)_4]^+$ (**6**) as the major product, while *cis*-$[RuCl_2(pta)_4]$ (**2**) was formed only in 25% yields. However, in an aqueous solution of **1** containing also 2.5 eq chloride, **2** was produced exclusively (Scheme 3) [34].

The observations of Romerosa and co-workers were supported by the results of Alessio et al who found the $\lambda = 470$ nm light optimal for inducing *trans* to *cis* (**1** to **2)** isomerization of $[RuCl_2(pta)_4]$. Different reactivities of **1** and **2** were also revealed in the reaction of these two complexes with bipyridine (bipy). When **1** was refluxed in water for 1 h together with 1 eq. bipyridine, only *mer*-$[Ru(bpy)Cl(pta)_3]Cl$ (**7**) was detectable in the solution. In contrast, even with 1.5 eq. bipy, **2** required 10 h reflux to undergo full conversion mostly to yield the same complex (**7**), however *fac*-$[Ru(bpy)Cl(pta)_3]Cl$ (**8**) was also formed as a byproduct. Whether the direct formation of **7** from **2** took place slowly or first it required a slow **2** to **1** isomerization followed by fast coordination of bipy, was not established [35].

The studies on reactions of **1** and **2** with bipy also revealed an important role of water as the solvent. Namely, the reactions, discussed in the preceeding paragraph, did not take place to an appreciable extent in organic solvents, such as chloroform or acetonitrile. Furthermore, in coordinating organic solvents it is the pta and not the chloride ligand which undergoes replacement by solvent molecules: in boiling dmso or acetonitrile *cis,mer-*



Scheme 4. Synthesis of Ru(II)-complexes with N-methyl-pta ligands.

$[RuCl_2X(pta)_3]$ (X = dmso, MeCN) were detected. In contrast, water is able to replace the coordinated chloride e.g. in **7** and **8** affording the corresponding aquocomplexes. It was argued, that in the studied organic solvents, solvation of chloride did not contribute sufficiently to the energetics of the reaction, and so the reactions involving chloride replacement had negligible thermodynamic drive [35]. Indeed, solvation of ionic or polar species may substantially influence certain reactions in aqueous solutions, especially those which include proton release. Perhaps the best known example is the heterolytic splitting of H_2 which is unfavorable in apolar organic solvents but becomes thermodynamicalliy favorable in aqueous systems [2,36–38].

Alessio et al synthesized *trans*-$[RuBr_2(pta)_4]$ (**9**), too, starting from $RuBr_3$ and following the synthetic route shown for **1** on Scheme 1. In aqueous solution, **9** is stable in the dark, but yields *cis*-$[RuBr_2(pta)_4]$ (**10**) upon exposure to light (λ = 470). In addition to isomerization, one or both chlorides may be replaced by molecules of the solvent with formation of *cis*-$[RuBr(H_2O)(pta)_4]^+$ (**11**), and *cis*-$[Ru(H_2O)_2(pta)_4]^{2+}$ (**12**), respectively (Scheme 3) [32].

cis-$[RuCl_2(pta\text{-}Me)_4](OTf)_4$ (**13**) was prepared by refluxing in the dark an ethanolic solution of $[RuCl_2(PPh_3)_3]$ in the presence of 5 eq. of (pta-Me)OTf (OTf = $CF_3SO_3^-$) [39]. This complex is also photoactive. Irradiation of **13** in aqueous solution (300 < λ less than 400 nm) led to the formation of *mer*,*trans*-$[RuCl_2(H_2O)(pta\text{-}Me)_3](OTf)_3$ (**14**). Interestingly, **14** was also obtained in a boiling solution of $[RuCl_2(PPh_3)_3]$ and 3 eq. (pta-Me)OTf (Scheme 4). Solid-state structures of **13** and **14** were determined by single-crystal X-ray diffraction. Reaction of **14** with 3 eq. chloride resulted in formation of $[RuCl_3(pta\text{-}Me)_3](OTf)_2$ (**15**), also characterized by SC-XRD [39]. Due to its photoactivity, **14** was tested as photosensitizer in dye-sensitized solar cells [40].

The iodo-analog of **14**, i.e. *mer*,*trans*-$[RuI_2(H_2O)(pta\text{-}Me)_3]I_3$ (**16**) was obtained in an aqueous solution of $RuCl_3$ and 5 eq. (pta-Me)I which also contained additional KI. With the use of only 3 eq. (pta-Me)I, the reaction afforded the neutral *trans*-$[RuI_4(pta\text{-}Me)_2]$ (**17**) (Scheme 4) [41].

The importance of the [ligand]/[Ru] ratio on the composition of the resulting complexes was also observed when a solution of $[RuCl_2(PPh_3)_3]$ in dichloromethane (or in toluene) was stirred with 4 or 3 eq. pta dissolved in water. In the first case, *trans*-$[RuCl_2(pta)_4]$ (**1**) was isolated from the aqueous phase, while with 3 eq. pta, the isolated product was *mer*,*trans*-$[RuCl_2(H_2O)(pta)_3]$ (**18**) [25]. With 1 eq. pta, fast water replacement in **18** furnished *trans*-$[RuCl_2(pta)_4]$ (**1**) quantitatively (Scheme 3), however, a similar H_2O/Cl^- ligand exchange required high chloride excess; even in the presence of 10 eq. chloride *mer*-$[RuCl_3(pta)_3]^-$ was obtained only in 20% yield. In a solution of **18** in 0.1 M aqueous HCl, ligand exchange and simultaneous protonation of the pta ligands resulted in formation of *mer*-$[RuCl_3(ptaH)_3]^{2+}$ (**19**) which isomerized to *fac*-$[RuCl_3(pta\text{-}H)_3]^{2+}$ (**20**) upon exposure to visible light (Scheme 3). The solid state structures of **19**$Cl_2{\cdot}2H_2O$ and **20**$Cl_2{\cdot}1.25H_2O$ were determined by SC-XRD. It was established, that in aqueous solution these complexes were in equilibrium with the respective *mer*- or *fac*-$[RuCl_2(H_2O)(ptaH)_3]^{3+}$ species [42].

In the reactions of aliphatic tertiary phosphines and hydrated $RuCl_3$ in boiling ethanol, in addition to (or instead of) mononuclear $[RuCl_2(PR_3)_{3\text{-}4}]$-type products, dinuclear complexes with the general formula $[\{Ru(PR_3)_3\}_2(\eta\text{-}Cl)_3]Cl$ are also formed [43]. However, in the case of pta, under the same reaction conditions we have never observed formation of anything else than *trans*-$[RuCl_2(pta)_4]$ (**1**). Conversely, heating an aqueous solution of *mer*,*trans*-$[RuCl_2(H_2O)(pta)_3]$ (**18**) to 80 °C, or irradiation of such a solution at room temperature with light (λ > 460 nm), leads to formation of $[\{Ru(pta)_3\}_2(\mu\text{-}Cl)_3]^+$ (**21**) (Scheme 3). The same complex ion was obtained when aqueous solutions of *cis*-$[RuCl_2(dmso)_4]$, *cis*,*trans*-$[RuCl_2(dmso)_2(pta)_2]$ or $[\{(\eta^6\text{-}p\text{-cymene})RuCl_2\}_2]$ were irradiated in the presence of pta (n_{pta}/n_{Ru} = 3). The structure of (**21**)$Cl{\cdot}9H_2O$ was established by SC-XRD showing unequivocally the dinuclear nature of the complex [42].

Obviously, a most useful Ru(II)-precursor for synthesis of water-soluble Ru(II)-complexes could be $[Ru(H_2O)_6](tos)_2$ (tos = tosylate) [28], itself synthesized from hydrated ruthenium(III) chloride. $[Ru(H_2O)_6]^{2+}$ allows building in various halides (or other anions) in place of the H_2O ligands, or preparation of catalysts for reactions which are inhibited by halide ions. However, this complex did not gain widespread application, most probably due to its cumbersome synthesis which also includes the need of handling volatile, reactive and toxic RuO_4. Furthermore, aqueous solutions of $[Ru(H_2O)_6](tos)_2$ are exceedingly oxygen sensitive, and at pH > 6 the complex decomposes due to the deprotonation of coordinated H_2O. Conversely, in acidic solutions, some prospective phosphine ligands may be protonated. For example, we have obtained a pK = 5.89 (T = 25.0 °C) for *N*-basicity of pta in aqueous HCl solutions with use of the pH-potentiometric titration method [44].

With these two possible effects in mind, the interaction of $[Ru(H_2O)_6](tos)_2$ and pta was investigated with ^{31}P NMR spectroscopy in aqueous solution at pH = 6, various [pta]/[Ru] ratios and temperatures. In the case of [pta]/[Ru] = 2 at room temperature, the major product was $[Ru(H_2O)_5(pta)]^{2+}$ (**22**) and Ru(II)-complexes containing more than one pta ligands could be detected only in traces. *Cis*- and *trans*-$[Ru(H_2O)_4(pta)_2]^{2+}$ (**23** and **24**, respectively), turned to be the major species only at a significantly higher ligand excess, [pta]/[Ru] = 15, however, even in that case, $[Ru(H_2O)_3(pta)_3]^{2+}$ (**25**) was present only in small concentration. Under these conditions, traces of *cis*-$[Ru(H_2O)_2(pta)_4]^{2+}$ (**26**), *cis*-$[Ru(H_2O)(OH)(pta)_4]^+$ (**27**), and the neutral *cis*-$[Ru(OH)_2(pta)_4]$ (**28**) were also observed. From more acidic solutions (pH = 4) *trans*-$[Ru(H_2O)_4(ptaH)_2](tos)_4{\cdot}2H_2O$ (**29**$\cdot\cdot 2H_2O$) could be isolated, which contain protonated pta ligands [44].

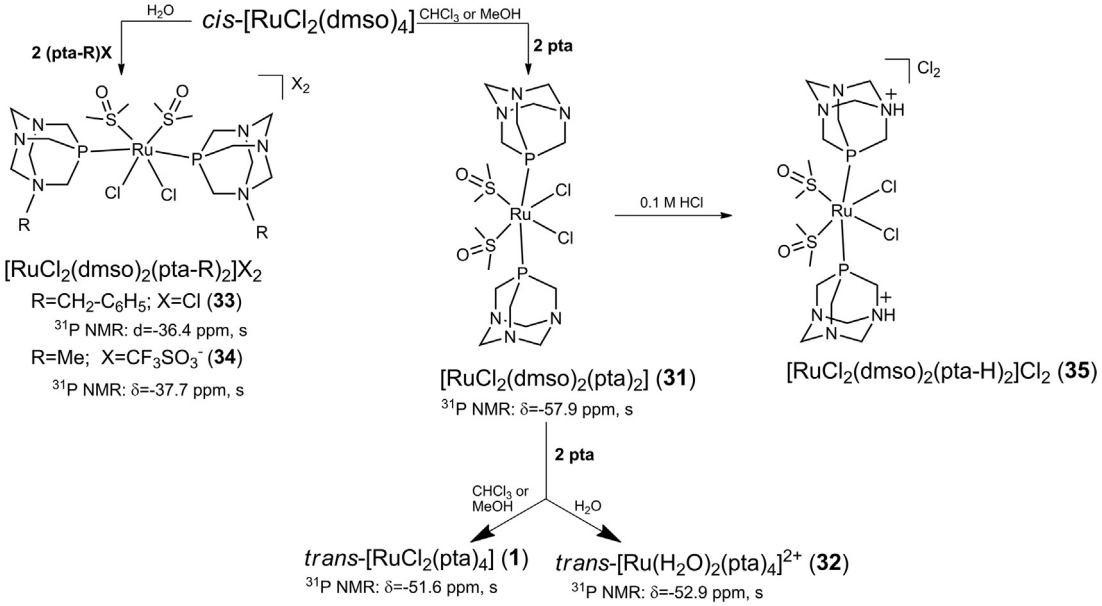
Single crystals of a Ru(II)-complex of similar structure, *trans*-$[Ru(H_2O)_4(pta\text{-}Me)_2](tos)_4{\cdot}2H_2O$ (**30**$\cdot\cdot 2H_2O$), were obtained from an aqueous solution of (pta-Me)(tos) and $[Ru(H_2O)_6](tos)_2$ at pH = 5.5. Reaction of (pta-Me)I and $[Ru(H_2O)_6](tos)_2$ in the presence of KI yielded *mer*,*trans*-$[RuI_2(H_2O)(pta\text{-}Me)_3]I_3{\cdot}2H_2O$ (**16**$\cdot\cdot 2H_2O$) [44]. This latter reaction (Scheme 4) proved faster and cleaner than a previously published procedure using hydrated $RuCl_3$ as starting material [41].

2.2. Synthesis of Ru(II)-complexes containing pta or its derivatives from Ru(II)-dmso precursors

Another well defined, water-soluble Ru(II)-complex, suitable for synthesis of Ru(II)-pta complexes, is *cis*,*fac*-$[RuCl_2(dmso\text{-}O)(dmso\text{-}S)_3]$ (*cis*-$[RuCl_2(dmso)_4]$, in short) which can be obtained by a few minutes reflux of hydrated $RuCl_3$ in dimethyl sulfoxide [26–27] (certainly a much simpler procedure than the synthesis of $[Ru(H_2O)_6](tos)_2$). Its isomer, *trans*-$[RuCl_2(dmso\text{-}S)_4]$ can also be simply prepared, by visible light irradiation of dmso solutions of hydrated $RuCl_3$ [27,45].

Upon dissolution of *cis*-$[RuCl_2(dmso)_4]$ in water, the *O*-coordinated dmso ligand is replaced by H_2O resulting in formation of *cis*,*fac*-$[RuCl_2(H_2O)(dmso\text{-}S)_3]$ [45]. In the presence of 1 eq. pta, only the replacement of the aquo ligand by the phosphine was expected, however, the ^{31}P NMR spectrum of the solution showed *cis*,*cis*,*trans*-$[RuCl_2(dmso)_2(pta)_2]$ (**31**) as the single product of the reaction (Scheme 5).

Exclusive formation of **31** was confirmed also by the observation of only one isosbestic point of the UV–vis spectra of solutions containing *cis*-$[RuCl_2(dmso)_4]$ and increasing amounts of pta (up to [pta]/[Ru] = 2). Conceivably, the first pta replaces the H_2O ligand



Scheme 5. Reactions of *cis*-[$RuCl_2(dmso)_4$] with pta and its N-alkyl derivatives [46].

and exerts a strong *trans*-labilizing influence on the opposite dmso, which largely facilitates coordination of a second pta ligand. As a consequence, the monophosphine Ru(II)-pta complex cannot be formed in detectable concentration [46].

Reactions of *cis*-[$RuCl_2(dmso)_4$] could be studied both in aqueous solutions and in polar organic solvents due to its sufficient solubility in such media. This feature also contributed to the versatile use of this compound as a starting material for water-soluble complexes with phosphine ligands, including pta and its derivatives, too (Scheme 5).

Both in chloroform [46] and methanol [35], the reaction of *cis*-[$RuCl_2(dmso)_4$] and 2 eq. pta resulted in exclusive formation of *cis,cis,trans*-[$RuCl_2(dmso)_2(pta)_2$] (**31**). In the presence of excess pta, **31** underwent a slow reaction (even at 50 °C temperature), however, no formation of a *tris*(pta)Ru(II) complex was observed, instead, the reaction yielded *trans*-[$RuCl_2(pta)_4$] (**1**) [46]. In contrast, in methanol, a fast reaction of *trans*-[$RuCl_2(dmso\text{-}S)_4$] and 4 eq. pta gave **1** (and only **1**) [35].

At temperatures above 40 °C, addition of 4 eq. pta into an aqueous solution of *cis*-[$RuCl_2(dmso)_4$] led to formation of a *tetrakis* (pta)Ru(II) complex, however, the ^{31}P NMR signal of the product did not match those of *trans*-[$RuCl_2(pta)_4$] and *cis*-[$Ru(H_2O)_2(pta)_4]^{2+}$. The product was identified as *trans*-[$Ru(H_2O)_2(pta)_4]^{2+}$ (**32**) which was supported by the appearance of the ^{31}P NMR resonance of *trans*-[$RuCl_2(pta)_4$] upon addition of at least 5 eq. chloride to a solution of **32** [46].

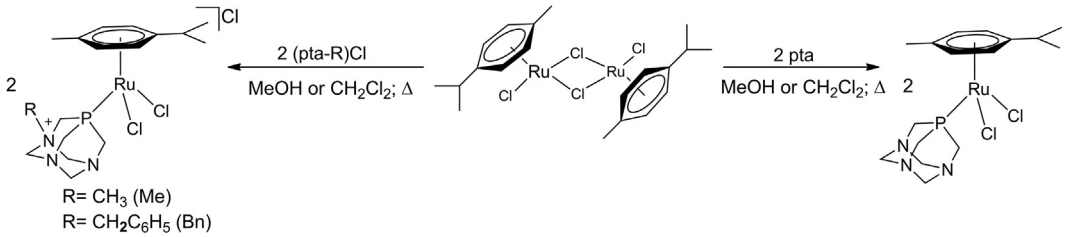
Addition of (pta-Bn)Cl or (pta-Me)CF_3SO_3 to aqueous solutions of *cis*-[$RuCl_2(dmso)_4$] also led to formation of cationic complexes. Note, that in the ^{31}P NMR spectra of the products, only resonances of *cis,cis,trans*-[$RuCl_2(dmso)_2(pta\text{-}R)_2]^{2+}$ were seen, even at n_P: $n_{Ru} > 2$ ratios.

From aqueous solutions of the products –characterized by multinuclear NMR and ESI-MS measurements– *cis,cis,trans*-[$RuCl_2(dmso)_2(pta\text{-}Bn)_2]Cl_2$ (**33**) and *cis,cis,trans*-[$RuCl_2(dmso)_2(pta\text{-}Me)_2](CF_3SO_3)_2$ (**34**) were isolated with 66% and 67% yield, respectively. Slow evaporation of the solvent from a methanolic solution of **34** allowed isolation of single crystals of the complex [46].

In the pH = 2.5–6.0 region, ^{31}P NMR spectra of aqueous solutions containing **33** or **34** remained unchanged, while the chemical shifts of the ^{31}P NMR signals of *cis,cis,trans*-[$RuCl_2(dmso)_2(pta)_2$] changed according to a sigmoid curve with the change of pH. Henderson-Hasselbach treatment of the data allowed determination of the protonation constant of the Ru(II)-coordinated pta as pK = 3.4. This value is significantly lower than the pK for the protonation of the free ligand, however, the trend is similar to the case of pta vs. the Ru(II)-bound pta in [(η^6-arene)$RuCl_2$(pta)] (to be discussed later) [47]. The product of protonation, *cis,cis,trans*-[$RuCl_2(dmso)_2(ptaH)_2]Cl_2$ (**35**) was isolated in form of single crystals, too (Scheme 5) [46].

2.3. (Arene)ruthenium(II) complexes containing pta or its derivatives

While the number of dmso-containing Ru(II)-pta complexes is small, half-sandwich Ru(II)- are numerous, and several of them were used as starting materials for the synthesis of (arene) ruthenium(II)-pta complexes [17–20]. A large group of such complexes contain the η^5-cyclopentadienyl ligand or its variously sub-



Scheme 6. Synthesis of [(η^6-*p*-cymene)$RuCl_2$(pta)] and [(η^6-*p*-cymene)$RuCl_2$(pta-R)]Cl complexes.

stituted derivatives. The majority of Cp'Ru(II)-pta complexes can be obtained by ligand exchange in [(η^5-Cp')Ru(P)$_2$Cl] (P = PPh_3, *m*tppms) upon the action of 1 or 2 eq. pta or pta-Me. An excellent review is available on CpRu(II)-pta complexes (Cp = $C_5H_5^-$) [48]. In general, the [(η^5-Cp')Ru(PPh_3)(pta)Cl]-type complexes where Cp': Cp [48–49]; Dp = $C_8H_9^-$; Ind = $C_9H_7^-$ [50]), and the [(η^5-Cp')Ru(pta)$_2$Cl]-type complexes where Cp': Cp, Cp* (Cp* = $C_5(CH_3)_5^-$) [51]; Dp [50]; Ind [52]), can be obtained with high yields.

In contrast to the procedures based on ligand exchange, [(η^6-arene)$RuCl_2$(P)] complexes (P = pta or derivatives) are synthesized almost exclusively from the appropriate [{(η^6-arene)$RuCl_2$}$_2$] dimers. For example, [(η^6-arene)$RuCl_2$(pta)] (arene = benzene [53]; *p*-cymene [54]) were obtained in the reaction of pta and [{(η^6-arene)$RuCl_2$}$_2$] (n_{Ru}:n_{pta} = 1:1) in methanol or dichloromethane solution (Scheme 6). Scheme 6 also shows the synthetic route to [(η^6-*p*-cymene)$RuCl_2$(pta-Me)]Cl [55], and [(η^6-*p*-cymene)$RuCl_2$(pta-Bn)]Cl [56–57].

Together with the synthesis of the first example of such complexes, [(η^6-*p*-cymene)$RuCl_2$(pta)] (**36**), Dyson and co-workers also reported the anticancer properties of this compound [54]. Later on, extensive studies were made with a large number of analog complexes in which either the aromatic ligands [58–60] or the anions [61–64] were changed systematically, with the biological activity of the complexes placed into the focus of research. A general name of these compounds, RAPTA, has been coined from Ru-Arene-PTA, and the antimetastatic properties of the various RAPTA-type Ru(II)-complexes have been under intensive recent scrutiny, too. The physiological effects of RAPTA-type complexes are summarized and discussed in various reviews [65–72], and will not be treated in this paper.

Of the half-sandwich Ru(II)-pta complexes, this review will mostly deal with [(η^6-*p*-cymene)$RuCl_2$(P)] (P = pta, (pta-Me)$^+$, (pta-Bn)$^+$) and [(η^6-benzene)$RuCl_2$(pta)]. These compounds can be easily obtained in situ, in the reaction of the air-stable pta (or its derivatives) with [{(η^6-arene)RuCl}$_2$(μ-Cl)$_2$] in aqueous solutions, even in air. The dinuclear Ru(II)-precursors can be purchased from commercial sources, but they are also easy to synthesize via $RuCl_3$-catalyzed disproportionation of 1,3-cyclohexadiene or α-terpinene (1-isopropyl-4-methyl-1,3-cyclohexadiene) [29–30]. Originally it was thought that aqueous solutions of the [{(η^6-arene)RuCl}$_2$(μ-Cl)$_2$] dimers contain [(η^6-arene)Ru(H_2O)$_3$]$^{2+}$ formed in a stepwise aquation process [73]. Later investigations have established, that depending on the pH and the chloride content of the solutions, other species such as [{(η^6-*p*-cymene)Ru}$_2$(OH)$_2$]$^{2+}$ and [{(η^6-*p*-cymene)Ru}$_2$(OH)$_3$]$^+$ may also be present [74–75].

Similar to [{(η^6-arene)RuCl}$_2$(μ-Cl)$_2$], the [(η^6-arene)$RuCl_2$(pta)] complexes may also undergo aquation in aqueous solution. This is supported by the observation of only one ^{31}P NMR signal in chloroform, but two in water, which refers to formation of [(η^6-arene)RuCl(H_2O)(pta)]$^+$. In the presence of chloride, aquation is suppressed [53]: in the presence of 100 eq. NaCl no [(η^6-arene)RuCl(H_2O)(pta)]$^+$, indispensable for the physiological effects, is present in the aqueous solutions [61]. Although in room-temperature aqueous solutions of [{(η^6-arene)$RuCl_2$}$_2$] and pta in [pta]:[Ru] = 2 ratio the major product is the expected [(η^6-arene)RuCl(pta)$_2$]$^+$, however, small amounts of [(η^6-arene)$RuCl_2$(pta)] and [(η^6-arene)RuCl(H_2O)(pta)]$^+$, together with *trans*-[$RuCl_2$(pta)$_4$] could be detected, too [53].

In an aqueous solution of [{(η^6-arene)RuCl}$_2$(μ-Cl)$_2$] + 3 pta under 100 bar H_2 pressure, various Ru(II)-hydridocomplexes were identified. In the first 180 min of the reaction, only the ^{1}H NMR signal of [(η^6-benzene)RuH(pta)$_2$]$^+$ was detected, but later on smaller intensity resonances of [(η^6-benzene)RuH(pta)X]$^{n+}$ (X = Cl^-, *n* = 0; X = H_2O, *n* = 1) species were also observed. Signals of [RuH(pta)$_4$-X]$^{n+}$ species (X = Cl^-, *n* = 0; X = H_2O, *n* = 1) [76] could be seen, too, however, the spectra did not show any sign of the presence of phosphine-free clusters, described by Süss-Fink [77]. Similar observations were made when [{(η^6-*p*-cymene)$RuCl_2$}$_2$] was used instead of [{(η^6-benzene)$RuCl_2$}$_2$].

Reactions of H_2 (100 bar) with either [(η^6-*p*-cymene)$RuCl_2$(pta)] + 2 pta or [{(η^6-*p*-cymene)$RuCl_2$}$_2$] + 6 pta, resulted in formation of the same Ru(II)-hydrides. In the first 6 h of the reaction, the main species observable by ^{1}H NMR measurements was [(η^6-*p*-cymene)RuH(pta)$_2$]$^+$. In addition, already in the second hour the known [76] [RuH(pta)$_4$X]$^{n+}$, [RuH_2(pta)$_4$], and [RuH(pta)$_5$]$^+$ species appeared, too, however, even after 20 h, the ratio of [(η^6-*p*-cymene)RuH(pta)$_2$]$^+$ among all the Ru(II) hydrides was as high as 50% [53].

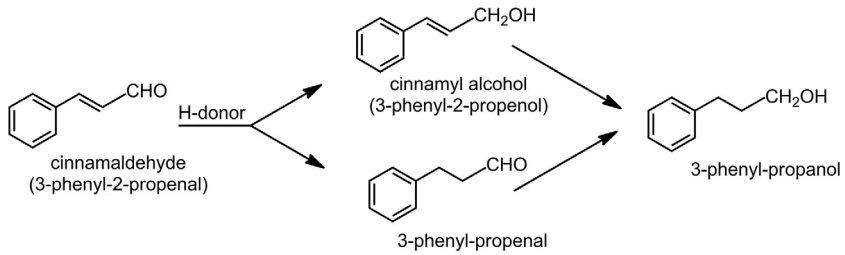
3. Catalytic applications of Ru(II)-pta complexes obtained from simple Ru(II)-precursors

Four reactions were chosen to illustrate the catalytic activity of Ru(II)-pta complexes in aqueous media. These are all characterized by the very simple way of catalyst synthesis starting from easily available Ru(II) precursors. Hydrogenation of CO_2 (HCO_3^-) takes place in purely aqueous solvent, while the other three reactions proceed in aqueous-organic biphasic reaction mixtures. From these, reduction of aldehydes by hydrogen transfer from aqueous formate was the first process in which a Ru(II)-pta complex was applied as the catalyst. Formate may take an important part in the Ru(II)-pta-catalyzed redox isomerization of allylic alcohols, too, facilitating formation of catalytically active Ru(II)-hydrido species. In the fourth reaction type discussed below, i.e. in the selective hydration of nitriles to amides, water not only plays the role of the solvent, but itself is one of the reaction partners.

3.1. Hydrogenation and transfer hydrogenation of aldehydes with phosphaurotropine-containing Ru(II)-complexes

Ru(II)-complexes having tertiary phosphine ligands are often applied as catalysts in hydrogenation reactions. Likewise, the first catalytic application of *trans*-[$RuCl_2$(pta)$_4$] (**1**) was attempted in the aqueous-organic biphasic hydrogenation of aldehydes. The first results were not very impressive. When a chlorobenzene solution of benzaldehyde was intensively stirred under 1 bar H_2 with a solution of *trans*-[$RuCl_2$(pta)$_4$] in an aqueous buffer at pH = 8, only 2% conversion of the aldehyde was observed in 5 h at 80 °C. This corresponds to a TOF = 0.06 h^{-1} (TOF=(mol converted substrate)×(mol catalyst × time)$^{-1}$). Under the same conditions, but with elevated hydrogen pressure (*P* = 30 bar), hydrogenation of benzaldehyde proceeded with 46% conversion (TOF = 11.6 h^{-1}) [25], still showing a modest catalytic activity [25].

Selective reduction of allylic aldehydes may furnish allylic alcohols which are important substances used in the food and fragrance industries. Relatively high catalytic activity could be observed in the hydrogenation of cinnamaldehyde (3-phenyl-2-propenal) (Scheme 3.1.1) with *trans*-[RuI_2(H_2O)(pta-Me)$_3$]I_3 (**16**) as the catalyst. The reaction took place in an aqueous-organic biphasic reaction mixture with H_2 of atmospheric pressure. Already at 20 °C temperature, a TOF = 4 h^{-1} was determined, but even more importantly, the reaction yielded cinnamyl alcohol (3-phenyl-2-propenol) as the sole product. Under increased H_2 pressure (*P* = 30 bar) and at elevated temperature (*T* = 60 °C) the turnover frequency reached 183 h^{-1}, however the higher reaction rate was accompanied by lower selectivity: in addition to 36% cinnamyl alcohol, 5% saturated aldehyde and 4% 3-phenyl-propanol was also obtained. Interestingly, under the same reaction conditions but with *trans*-[RuI_4(pta-Me)$_2$] (**17**) as the catalyst, the major product



Scheme 3.1.1. Hydrogenation of cinnamaldehyde.

Table 3.1.1
Reduction of various aldehydes by hydrogen transfer from aqueous HCOONa catalyzed by *trans*-[$RuCl_2(pta)_4$] and [{$RuCl(m$tppms-$Na)_2$}$_2$(μ-$Cl)_2$]. (data from Refs. [25,78,79]) .

Aldehyde	TOF (h^{-1})[a]	
	trans-[$RuCl_2(pta)_4$][b]	Ru-*m*tppms[c]
Benzaldehyde	92	133
4-Me-Benzaldehyde	23.6	132
4-MeO-Benzaldehyde	26.7	131
4-Br-Benzaldehyde	16.3	133
2-OH-Benzaldehyde	0	0
Cinnamaldehyde	30.0[d]	131[d,e]

Conditions: a) determined by GC; b) 0.0625 mmol *trans*-[$RuCl_2(pta)_4$], 1.35–6.93 mmol aldehyde, 5 mL aqueous 5 M HCOONa, 5 mL chlorobenzene, T = 80 °C, t = 3 h; c) 0.005 mmol [{$RuCl(m$tppms-$Na)_2$}$_2$(μ-$Cl)_2$], n(aldehyde):n(*m*tppms):n(Ru) = 200:2:1, 3 mL aqueous 5 M HCOONa, T = 80 °C, t = 1.5 h; d) exclusively unsaturated alcohol product; e) t = 2 h.

(84%) was the saturated aldehyde, together with 5% 3-phenyl-propanol, however, no cinnamyl alcohol was found in the product mixture. The reaction rate was also lower (TOF = 40 h^{-1}) than with **16** as the catalyst [41].

Peruzzini and co-workers also observed the preferential hydrogenation of C = C bond in the reduction of an α,β-unsaturated ketone, benzylideneacetone, catalyzed by [(η^5-arene)Ru(pta)$_2$Cl] complexes [51]. Although a detailed discussion of the properties of [(η^5-Cp*)Ru(pta)$_2$Cl] and [(η^5-Cp)Ru(pta)$_2$Cl] complexes is not intended in this review, some of the characteristic features of their catalytic properties are worth mentioning. For example, while the temperature dependence of the catalytic activity of [(η^5-Cp)Ru(pta)$_2$Cl] was found high, that of [(η^5-Cp*)Ru(pta)$_2$Cl] proved negligible. Consequently, while at 80 °C [(η^5-Cp*)Ru(pta)$_2$Cl] showed approximately 50% higher activity than [(η^5-Cp)Ru(pta)$_2$Cl], the order reversed at 130 °C [51]. From the pH-dependence of the reaction rate of benzylideneacetone hydrogenation Frost and Mebi concluded that the conversion varied parallel to the concentration of the conceived catalytically active species, [(η^5-Cp)RuH(pta)(ptaH)]$^+$; maximum conversion was achieved at pH = 4.7, corresponding to TOF = 19.4 h^{-1} [77].

In comparison, *trans*-[$RuCl_2(pta)_4$] (**1**) was found less active than [{$RuCl(m$tppms-$Na)_2$}$_2$(μ-$Cl)_2$] in transfer hydrogenation of aldehydes from 5 M aqueous HCOONa (Table 3.1.1). In contrast to the low catalytic activity of **1** under 1 bar H_2 [25], in basic solutions the Ru(II)-*m*tppms catalyst hydrogenated cinnamaldehyde to cinnamyl alcohol with high yield and exclusive selectivity [37–38].

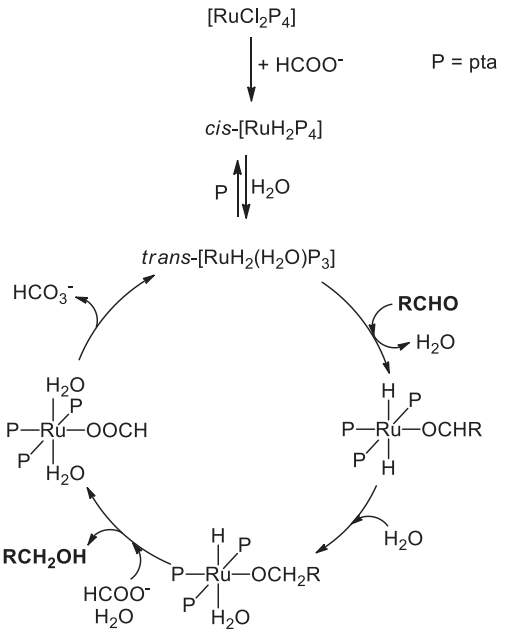
Both catalysts proved inactive in the hydrogen transfer reduction of salicylaldehyde which is probably caused by strong coordination of this substrate to the Ru(II) central ion of the complexes. The catalytic efficiency of *trans*-[$RuCl_2(pta)_4$] (**1**) was investigated also in the hydrogen transfer reduction of $CH_3(CH_2)_nCHO$ aliphatic aldehydes, where it was found that the conversions decreased with increasing chain length (which also caused decreasing water-solubility of the substrates): n = 1, 81.6%; n = 2, 72.8%; n = 3, 46.1%; n = 5, 23.0%) [25].

The catalytic activities of various Ru(II)-pta complexes are shown by the data of Table 3.1.2. It can be seen, that in hydrogenation of benzaldehyde the dmso-ligated *cis,cis,trans*-[$RuCl_2(dmso)_2(P)_2$] (P = pta, **31**; pta-Bn, **33**; pta-Me, **34**) catalysts showed lower activity than *trans*-[$RuCl_2(pta)_4$] (**1**) (entries 6–7-8 vs 1). Although in hydrogenation of cinnamaldehyde their activity was found higher than that of **1**, however, this was accompanied by incomplete (**33**, **34**) or poor (**31**) selectivity to cinnamyl alcohol [42]. In contrast, the reduction of cinnamaldehyde with *trans*-[$RuCl_2(pta)_4$] as the catalyst produced exclusively the desired cinnamyl alcohol (**A**) [42]. Note, that these experiments were carried out under normal daylight conditions with no efforts to exclude light [25].

Table 3.1.2
Reduction of benzaldehyde and cinnamaldehyde with hydrogen transfer from aqueous HCOONa catalyzed by various Ru(II)-pta complexes (**A**: cinnamyl alcohol, **B**: 3-phenyl-propanal; **C**: 3-phenyl-propanol) ([25,42]).

Entry	Catalyst	Benzaldehyde	Cinnamaldehyde			
		Benzylalcohol (%)	Conversion (%)	Product yield (%)[a]		
				A	**B**	**C**
1	*trans*-[$RuCl_2(pta)_4$]	92	30	30	–	–
2	*trans*-[$RuCl_2(pta)_4$] + 5 eq. NaCl	90	29	29	–	–
3	*cis* -[$RuCl_2(pta)_4$]* (contains also *cis*-[$RuCl(H_2O)(pta)_4$])	85	32	24	5	3
4	*cisz*-[$RuCl_2(pta)_4$] * + 5 eq. NaCl	91	29	28	1	–
5	*mer,trans*-[$RuCl_2(H_2O)(pta)_3$]	99	55	55	–	–
6	*cis,cis,trans*- [$RuCl_2(dmso)_2(pta)_2$]	71	34	16	7	11
7	*cis,cis,trans*- [$RuCl_2(dmso)_2$(pta-Bn)$_2$]$^{2+}$	68	33	28	2	3
8	*cis,cis,trans*- [$RuCl_2(dmso)_2$(pta-Me)$_2$]$^{2+}$	78	40	36	2	2

Reaction conditions: n(Ru) = 0.0625 mmol, n(benzaldehyde) = 4.92 mmol, n(cinnamaldehyde) = 3.96 mmol, 5 mL aqueous 5 M HCOONa, 5 mL chlorobenzene, T = 80 °C, t = 3 h.
*Obtained by 20 min irradiation of an aqueous solution of *trans*-[$RuCl_2(pta)_4$] (halogen lamp, 150 W); a) determined by gas chromatography.



Scheme 3.1.2. Suggested mechanism of the reduction of aldehydes with hydrogen transfer from aqueous formate.

Discovery of the photoreactivity of *trans*-[$RuCl_2(pta)_4$] [34] initiated a repeated investigation of aldehyde reductions with this complex as the catalyst, now with careful exclusion of light. However, the conversions did not differ from those achieved under daylight [42]. In contrast, when aqueous solutions of *trans*-[$RuCl_2(pta)_4$] were irradiated for 20 min with visible light (150 W halogen lamp) and the resulting mixture of *cis*-[$RuCl_2(pta)_4$] and *cis*-[$RuCl(H_2O)(pta)_4]^+$ was used as catalyst for the transfer hydrogenation, benzaldehyde was reduced with decreased conversion, while the hydrogenation of cinnamaldehyde proceeded with lower selectivity (entries 3 vs 1 in Table 3.1.2). Most probably, these changes can be associated with the presence of *cis*-$[RuCl(H_2O)(pta)_4]^+$, since addition of chloride (i.e. transformation the aquo complex to *cis*-[$RuCl_2(pta)_4$]) led to conversion practically equal to that observed with the *trans*-[$RuCl_2(pta)_4$] catalyst (entries 4 vs 2) [42].

The initial rate of benzaldehyde reduction with *trans*-[$RuCl_2(pta)_4$] as the catalyst was found to increase with increasing catalyst concentration, and showed saturation as a function of the Na-formate concentration at $\geq$ 2.5 M. The same kinetic behaviour was observed with the use of the [{RuCl(*m*tppms-$Na)_2\}_2(\mu$-$Cl)_2$] catalyst, and the apparent activation energies, determined for the reactions with these two catalysts were also very close: E_a = 100.0 kJ $\times$ mol^{-1} for *trans*-[$RuCl_2(pta)_4$] [25], and E_a = 97.9 kJ $\times$ mol^{-1} for [{RuCl(*m*tppms-$Na)_2\}_2(\mu$-$Cl)_2$] [79]. (It is important to consider that in this –and similar– biphasic systems, changes in the temperature may effect not only the intrinsic rate of the reactions but also the solubilities of the substrates in the two phases, which in turn may bring about further changes in the observed reaction rate.) In contrast to the rate increasing effect of added *m*tppms in case of the [{RuCl(*m*-tppms-$Na)_2\}_2(\mu$-$Cl)_2$] catalyst [79], with *trans*-[$RuCl_2(pta)_4$] a 10-fold excess of pta practically stopped the reduction of benzaldehyde (TOF = 0.1 h^{-1}) [25]. This phenomenon refers to an important role of *tris*(pta)Ru(II) species in the catalytic cycle, which is further supported by the high catalytic activity of *mer,trans*-[$RuCl_2(H_2O)(pta)_3$] surpassing that of *trans*-[$RuCl_2(pta)_4$] (entry 5 vs 1, Table 3.1.2) [42]. Furthermore, it should be mentioned, that from a methanolic solution containing both *trans*-[$RuCl_2(pta)_4$] and HCOONa, *cis*-[$RuH_2(pta)_4$] was isolated [33]. Based on the above findings, the catalytic cycle depicted in Scheme 3.1.2 was suggested [42].

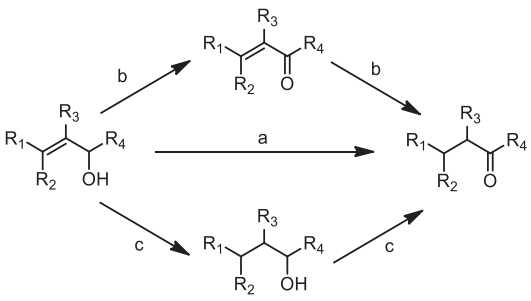
The role of the real catalytic species in this mechanism is played by [$RuH_2(H_2O)(pta)_3$]. Its formation from *cis*-[$RuH_2(pta)_4$] involves phosphine dissociation, which may be facilitated by the strong *trans*-labilizing effect of the hydrido ligands. Such loss of a phosphine ligand from the coordination sphere is in agreement with the rate decreasing effect of excess pta. Formate plays a role both in the formation and in the regeneration of the true catalytic species [$RuH_2(H_2O)(pta)_3$], again in agreement with the acceleration of the reaction and its eventual levelling off with increasing formate concentration. It is mentioned here, that [$RuCl_2(CO)(pta)_3$] proved completely inactive for catalysis of hydrogen transfer from aqueous formate to aldehydes, however, no detailed studies were made to rationalize this finding [25].

3.2. Redox isomerization and reduction of allylic alcohols in aqueous systems

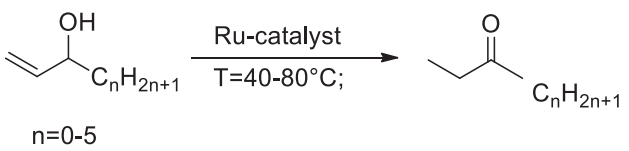
3.2.1. Phosphaurotropine-containing Ru(II)-halido, and (dmso)Ru(II)-complexes as catalysts

Traditionally, synthesis of ketones from allylic alcohols is made via sequential oxidation and hydrogenation steps (route *b* on Scheme 3.2.1) or in the reverse order, hydrogenation followed by oxidation (route *c*). In several cases, these processes (especially oxidation) require toxic or strongly corrosive reagents. Direct redox isomerization of allylic alcohols (route *a*) yields ketones in a simpler and environmentally safer way.

Several homogeneous catalysts are known for redox isomerization of allylic alcohols, however, the majority of them dissolve only in organic solvents [80–81]. Recently, much effort has been put into investigation of such processes in aqueous systems [82–85]. One of the first reports described successful isomerization of water-soluble, short-chain allylic alcohols with [$Ru(H_2O)_6$]$(tos)_2$ as the catalyst at 25–45 °C, and details of the reaction mechanism were also scrutinized [86]. In aqueous solutions, [{RuCl(*m*tppms-$Na)_2\}_2(\mu$-$Cl)_2$] and [(η^5-Cp)Ru(*m*tppms-$Na)_2$Cl] proved to be efficient catalysts for isomerization of CH_2 = $CHC(OH)(CH_2)_nCH_3$ (n = 0–5) to the corresponding ketones in argon atmosphere, at 40–80 °C (Scheme 3.2.2). The reaction rates varied as a function of the pH of the aqueous reaction mixture and in the case of the

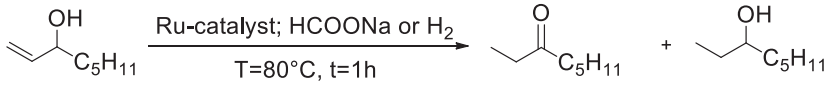


Scheme 3.2.1. Reaction of allylic alcohols to ketones in sequential oxidation/reduction steps (*b* or *c*) and via redox isomerization (*a*).



Scheme 3.2.2. Isomerization of 1-alken-3-ols with water-soluble Ru(II)-complex catalysts [87].

Table 3.2.1
Redox isomerization of 1-octen-3-ol catalyzed by *cis*-[$RuCl_2(dmso)_4$] and various Ru(II)-pta complexes [46]



Catalyst	Yield (%)			
	HCOONa*		H_2**	
	octan-3-one	octan-3-ol	octan-3-one	octan-3-ol
cis-[$RuCl_2(dmso)_4$]	96	0	83	2
[$RuCl_2(dmso)_2(pta)_2$] (**31**)	47	8	6	1
[$RuCl_2(dmso)_2$(pta-Me)$_2$](OTf)$_2$ (**34**)	51	14	7	2
[$RuCl_2(dmso)_2$(pta-Bn)$_2$]Cl_2 (**33**)	37	6	4	1
trans-[$RuCl_2(pta)_4$] (**1**)	6	0	0	0

Reaction conditions: n(Ru) = 0.01 mmol, n(1-octen-3-ol) = 0.50 mmol, 3 mL water, 3 mL toluene, *T* = 80 °C, t = 1 h; *n(HCOONa) = 0.50 mmol, **p(H_2) = 1 bar.

half-sandwich Ru(II)-complex the highest turnover frequency was TOF_{max} = 2220 h^{-1} [87].

In contrast to [{RuCl(*m*tppms-Na)$_2$}$_2$(μ-Cl)$_2$], *trans*-[$RuCl_2(pta)_4$] and the *cis,cis,trans*-[$RuCl_2(dmso)_2(P)_2$] (**31**, **33**, **34**) complexes catalyzed the redox isomerization of allylic alcohols only in presence of H_2 or $HCOO^-$ (Table 3.2.1). Furthermore, complexes **31**, **33**, **34** proved less active and selective, than their precursor *cis*-[$RuCl_2(dmso)_4$], although –in general– the presence of tertiary phosphines within the catalysts' coordination sphere increases the catalytic activity of Ru(II)-complexes. For example, in the presence of HCOONa, isomerization of 1-octen-3-ol with *cis*-[$RuCl_2(dmso)_4$] as the catalyst, yielded exclusively octan-3-one with high conversion (96%). The reaction remained selective to formation of octan-3-one with the *trans*-[$RuCl_2(pta)_4$] catalyst, too, however, the yield dropped sharply (6%). On the effect of the *cis,cis,trans*-[$RuCl_2(dmso)_2(P)_2$] (P = pta, **31**; pta-Bn, **33**; pta-Me, **34**) catalysts, the reaction proceeded with moderate conversions (43–65%), however the product mixture contained a large proportion (15–21%) of octan-3-ol [46].

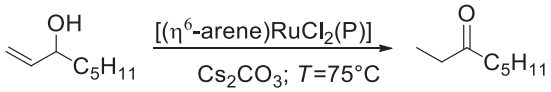
The high activity and selectivity of the *cis*-[$RuCl_2(dmso)_4$] catalyst was also demonstrated by exclusive formation of the corresponding ketones in the redox isomerization of 1-hepten-3-ol, 1-hexen-3-ol, and 1-penten-3-ol. Under conditions of Table 3.2.1, the conversions of the C7 and C6 allylic alcohols were close to quantitative, but only 69% in case of 1-penten-3-ol [46].

When Na-formate was replaced by hydrogen gas of ambient pressure, catalysis of the redox isomerization of 1-octen-3-ol by *cis*-[$RuCl_2(dmso)_4$] still yielded to 83% octan-3-one, however, this was accompanied by a small amount (2%) of the hydrogenated product, octan-3-ol. With the use of isolated, well-defined [$RuCl_2(dmso)_2(P)_2$] (**31**, **33**, **34**) catalysts, the yield of octan-3-one dropped to a few %; the same results were obtained with catalysts prepared in situ from *cis*-[$RuCl_2(dmso)_4$] and pta, (pta-Bn)Cl, (pta-Me)(OTf)$_3$, respectively. Under H_2, *trans*-[$RuCl_2(pta)_4$] (**1**) proved completely ineffective (Table 3.2.1) [46]. Obviously, addition of pta or its N-substituted derivatives to *cis*-[$RuCl_2(dmso)_4$] adversely effects the redox isomerization of allylic alcohols.

3.2.2. Phosphaurotropine-containing (arene)Ru(II)-complexes as catalysts

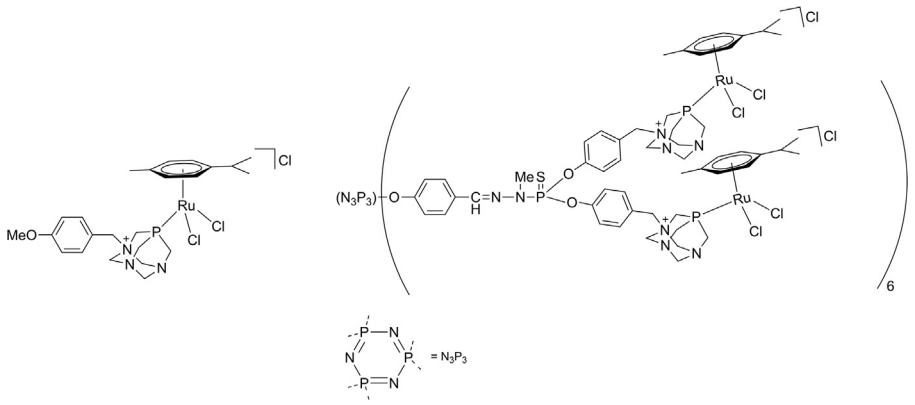
In general, the [(η^6-arene)$RuCl_2(P)$]-type complexes (arene = benzene, *p*-cymene, hexamethylbenzene; P = water-soluble phosphine) efficiently catalyze redox isomerization of allylic alcohols in the presence of bases [55,88–93]. As a specific example, 1-octen-3-ol was successfully isomerized to octan-3-one with [(η^6-*p*-cymene)$RuCl_2$(pta)] as the catalyst in aqueous solution at pH > 9, and the reaction proceeded in an inert atmosphere, too [93]. 1-Octen-3-ol is often used for studies of redox isomerization, in most cases under the reaction conditions introduced by Gimeno and co-workers, when the aqueous phase of the reaction mixture contained 1 mol% [(η^6-arene)$RuCl_2(P)$] and 2 mol% Cs_2CO_3, while 1-octen-3-ol was dissolved in tetrahydrofuran (THF) [88]. Efficiency of the catalysts can be best described by the TOF values, since in several cases different bases or different [substrate]/[catalys] ratios were used. Table 3.2.2 shows some of the results with Ru(II) catalysts containing pta, *N*-alkyl

Table 3.2.2
Activities of [(η^6-arene)$RuCl_2(P)$] complexes (P = water-soluble or Merrifield resin-immobilized phosphine) in aqueous-organic biphasic redox isomerization of 1-octen-3-ol (T = 75 °C).

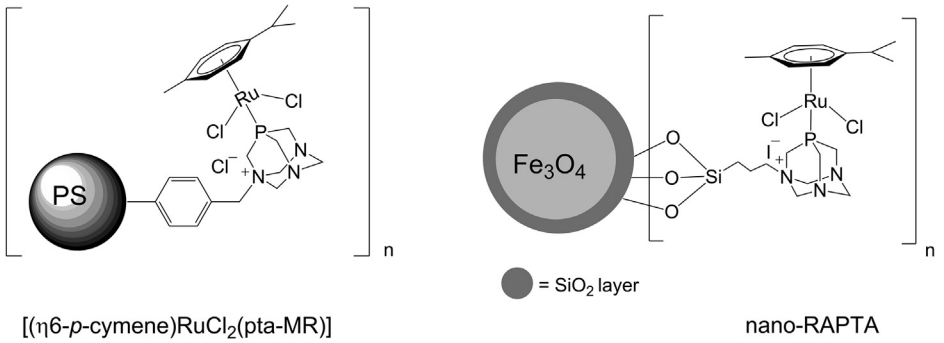


Entry	Ru(II)-complex	X in X_2CO_3	*t* (h)	TOF (h^{-1})	Ref.
1	[(η^6-*p*-cymene)Ru(η^2-O_2CO)(pta)]	–	0.5	396	[93]
2	[(η^6-*p*-cymene)$RuCl_2$(pta)]	Na	1	188	[93]
3	[(η^6-*p*-cymene)$RuCl_2$(pta-Bn)]Cl	Na	1	48	[*]
4	[(η^6-*p*-cymene)$RuCl_2$(pta-MR)]**	Na	3	14	[*]
5	[(η^6-*p*-cymene)$RuCl_2$(pta-{MeO-Bn})]Cl	Cs	8	3	[90]
6	[(η^6-*p*-cymene) $RuCl_2${P($CH_2OH)_3$}]	Cs	2.25	44	[88]
7	[(η^6-C_6Me_6)$RuCl_2${P($CH_2OH)_3$}]	Cs	3.5	29	[88]
8	[(η^6-benzene)$RuCl_2${P($CH_2OH)_3$}]	Cs	1.5	67	[88]
9	[(η^6-benzene)$RuCl_2$(pta-Me)]Cl	K	24	8	[55]

*unpublished results; **(pta-MR) = Merrifield resin-immobilized pta.



Scheme 3.2.3. [(η^6-*p*-cymene)$RuCl_2$(pta-{MeO-Bn})]Cl and its immobilized version supported on a 1st generation dendrimer [91].



Scheme 3.2.4. [(η^6-*p*-cymene)$RuCl_2$(pta)] supported on Merrifield resin (MR) and on silica-coated ferrite nanoparticles (nano-RAPTA).

pta-derivatives, or $P(CH_2OH)_3$ frequently applied by Gimeno and co-workers.

Depending on the arene ligand, [(η^6-arene)$RuCl_2${$P(CH_2OH)_3$}] catalysts were characterized by TOF values of 29–67 h^{-1} (entries 6–8) [88], the most active being the benzene-containing complex. Cadierno and Crochet replaced $P(CH_2OH)_3$ with *N*-methyl-pta, however this led to a drop of the TOF to 8 h^{-1} (entry 9). [(η^6-benzene)$RuCl_2$(pta-Me)]Cl was immobilized on Montmorillonite K-10 clay, and successfully used in this heterogenized form for isomerization of allylic alcohols in organic solvents [55]. Caminade and co-workers alkylated pta with *4*-methoxybenzyl chloride and used the product pta-(MeO-Bn)Cl to obtain [(η^6-*p*-cymene)$RuCl_2$(pta-{MeO-Bn})]Cl. With this catalyst they determined TOF = 3 h^{-1} in redox isomerization of 1-octen-3-ol (entry 5). The efficiency of this complex (conversion: 38%) was compared with the activity of [(η^6-*p*-cymene)$RuCl_2$(pta)] anchored onto a dendrimer with -O-$C_6H_5CH_2Cl$ end groups (Scheme 3.2.3) and a positive dendritic effect was determined (conversion: 98% with a 3rd generation dendrimer) [89–91].

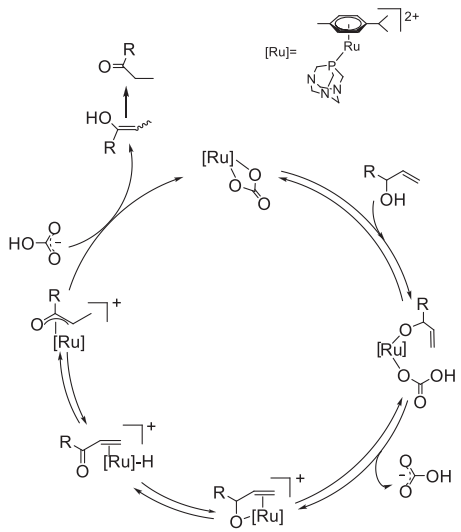
Although [(η^6-*p*-cymene)$RuCl_2$(pta-Bn)]Cl was found significantly more active (Table 3.2.2, entry 3; TOF = 48 h^{-1}) than [(η^6-*p*-cymene)$RuCl_2$(pta-{MeO-Bn})]Cl, unfortunately it did not show sufficient stability. Recirculation experiments revealed, that in the second and third runs, each, the activity decreased to its half, and in the fourth recycle, it dropped to a mere 2%.

By analogy to the synthesis of [(η^6-*p*-cymene)$RuCl_2$(pta-Bn)]Cl, we immobilized the complex on Merrifield resin (MR) via the reaction of pta with the chloromethyl-phenyl groups of the support, followed by the reaction of the such immobilized pta with [{(η^6-*p*-cymene)$RuCl_2$}$_2$] dissolved in chloroform (Scheme 3.2.4). Comparison of the activity of [(η^6-*p*-cymene)$RuCl_2$(pta-Bn)]Cl and the resin-immobilized [(η^6-*p*-cymene)$RuCl_2$(pta-MR)] catalysts showed that the latter retained about 30% of the activity of the homogeneous catalyst (entry 4; TOF = 14 h^{-1}). Such a drop of activity could be anticipated considering the heterogeneous nature of [(η^6-*p*-cymene)$RuCl_2$(pta-MR)]. However, immobilization made the catalyst markedly stable for recycling: the 92% conversion determined in the first three cycles was followed by 90% in the fourth and even in the fifth run.

[(η^6-*p*-cymene)$RuCl_2$(pta)] also showed appreciable catalytic activity (Table 3.2.2, entry 2; TOF = 47 h^{-1}), furthermore, this efficiency was retained even after the fifth recycle [93]. When Na_2CO_3 was added to an aqueous solution of this complex, the originally orange yellow solution turned lemon yellow as the consequence of formation of [(η^6-*p*-cymene)Ru(η^2-O_2CO)(pta)]. The latter carbonato-complex was isolated as single crystals, too, and its structure was determined by SC-XRD measurements [93].

Among the catalysts investigated, [(η^6-*p*-cymene)Ru(η^2-O_2CO)(pta)] displayed outstanding catalytic activity for redox isomerization of 1-octen-3-ol. In aqueous solution at 75 °C, in the absence of added base, a conversion of 99% was achieved already in 0.5 h (Table 3.2.2, entry 1; TOF = 396 h^{-1}). Poorly water-soluble, shorter-chain allylic alcohols, H_2C=CH-CH(OH)-$(CH_2)_n$-CH_3 (n = 1–3), yielded the corresponding ketones with 93–97% conversion, however, in the case of the water-soluble 1-propen-3-ol and 1-buten-3-ol, the conversions were only 24% and 27%, respectively. Interestingly, the catalytic activity of [(η^6-*p*-cymene)$RuCl_2$(pta)] in the presence of 2 equivalents of Na_2CO_3, reached only about 47% of that of the pre-formed [(η^6-*p*-cymene)Ru(η^2-O_2CO)(pta)] with no added base (entries 1 vs 2).

The suggested reaction mechanism (Scheme 3.2.5) implies deprotonation of the substrate allylic alcohol by the coordinated carbonate in the catalyst leading to formation of an alkoxy intermediate. Coordination of the enolate C = C bond simultaneously



Scheme 3.2.5. Suggested mechanism of redox isomerization of allylic alcohols catalyzed by [(η^6-*p*-cymene)Ru(η^2-O_2CO)(pta)] [93].

with decoordination of a bicarbonate results in formation of an η^3-oxo-allyl intermediate. Internal rearrangements, and protonation by bicarbonate would liberate the vinyl alcohol product (which spontaneously isomerizes to the saturated ketone) and, simultaneously, the [(η^6-*p*-cymene)Ru(η^2-O_2CO)(pta)] catalyst is regenerated.

It is important to recall here, that in this so-called η^3-oxo-allyl mechanism [81], proton concentration plays a double role. Deprotonation of allylic alcohols to enolates is facilitated by bases, while the release of the product from the η^3-oxo-allyl intermediate requires protonation. The carbonate ligand of the [(η^6-*p*-cymene)Ru(η^2-O_2CO)(pta)] catalyst is suitable to act as such a proton shuttle, and the close to neutral (pH = 7.2) aqueous solution of the complex is a most acceptable medium for isomerization of base-sensitive allylic alcohols [93].

Allylic alcohols were isomerized also in the absence of bases with microwave activation at 150 ^{0}C with the use of the catalyst dubbed nano-RAPTA (Scheme 3.2.4). This catalyst was prepared by *N*-alkylation of pta with (3-iodo-propyl)trimethoxysilane, followed by adsorption of the product onto silica-coated Fe_3O_4 nanoparticles and, finally, reacting this immobilized pta with [{(η^6-*p*-cymene)$RuCl_2$}$_2$] in a methanolic solution [92].

The isomerization reactions were carried out with neat substrates, in the presence of water with 1.58 mol % of the immobilized Ru(II)-catalyst. Of the H_2C=CH-CH(OH)-$(CH_2)_n$-CH_3 series only 1-octen-3-ol and 1-penten-3-ol were studied, and high catalytic activities were recorded in both cases (TOF = 257 h^{-1}, and 127 h^{-1}, respectively). Due to the magnetic properties of the Fe_3O_4 support, nano-RAPTA could be easily recycled, however, its catalytic activity decreased from cycle to cycle. For example, in the redox isomerization of 1-octen-3-ol, the TOF in the first run was 257 h^{-1}, however this value dropped to TOF = 7 h^{-1} in the 4th cycle. The catalytic activity of [(η^6-*p*-cymene)$RuCl_2$(pta)] was compared to its immobilized counterpart under the same reaction conditions. In the first cycle the soluble catalyst showed almost the same efficiency than nano-RAPTA, however, its activity decreased faster from cycle to cycle than that of its heterogenized variant [92]. This approach of isomerization of allylic alcohols demonstrates several aspects of green chemistry. In the isomerization reactions no organic solvent was applied, the reactions were activated with the use of an alternative energy source, and the catalyst was designed to be easily removable and ready to recycle.

The importance of aquocomplexes in redox isomerization of allylic alcohols is illustrated by the example of (η^5-Cp)Ru-phosphine complexes. It was established, that upon dissolution in water, [(η^5-Cp)Ru(pta)$_2$Cl] underwent ligand exchange and yielded [(η^5-Cp)Ru(pta)$_2$(H_2O)]$^+$ [50]. Such aquation process did not take place in cases of [(η^5-Cp)Ru(*m*tppms-Na)$_2$Cl] and [(η^5-Cp)Ru(pta-Me)$_2$Cl](OTf)$_2$. In contrast, the corresponding aquocomplexes (which were isolated in solid form, too) proved considerably more active in redox isomerization of allylic alcohols than their chloro-analogs. For example, at pH = 4.75, [(η^5-Cp)Ru(pta-Me)$_2$(H_2O)](OTf)$_3$ catalyzed the isomerization of 1-octen-3-ol with a TOF_{max} = 162 h^{-1}, while with [(η^5-Cp)Ru(pta-Me)$_2$Cl](OTf)$_2$ as the catalyst, only TOF = 10 h^{-1} was achieved [94]. An advantageous feature of [(η^5-Cp)Ru(pta)$_2$(H_2O)]OTf is in that it is capable to catalyze redox isomerization of CH_2=CHC(OH)$(CH_2)_n$$CH_3$ (n = 0–4) substrates with high efficiency even in air [95]. [(η^5-Cp)Ru(pta)$_2$(H_2O)]OTf deserves special attention also for its role played in establishing the reaction mechanism and the influence of water. In a recent study on the redox isomerization of 1-propen-3-ol with [(η^5-Cp)Ru(pta)$_2$(H_2O)]OTf as the catalyst, an intermediate Ru(II)-complex was identified by various experimental techniques (NMR, total neutron scattering). The data showed preferential solvation of some parts of the molecule; this finding was supported by quantum chemical calculations, too [96].

3.2.3. Mixed ligand (arene)ruthenium(II)–NHC-pta complexes as catalysts

Carbenes comprise a most important group of ligands for transition metals, due to their extreme versatility and the high stability of their complexes [97–100]. Not surprisingly, such catalysts have been employed also in catalysis of allylic alcohol redox isomerization.

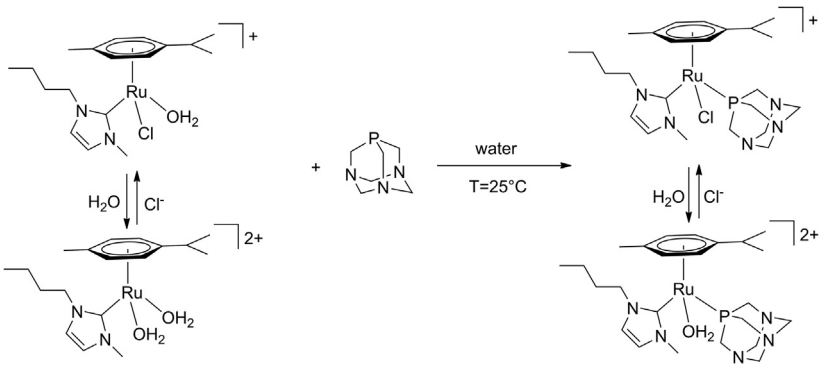
In an attempted hydrogenation of 1-propen-3-ol to 1-propanol with an [(η^6-*p*-cymene)$RuCl_2$(bmim)] (bmim = 1-butyl-3-methyl-imidazol-2-ylidene) catalyst, intermediate formation of acetone was observed (Scheme 3.2.6) [101]. It was found, that this complex catalyzed the redox isomerization of 1-alken-3-ols in water only in the presence of H_2 or formate salts. From reaction of an equimolar amount of pta and [(η^6-*p*-cymene)$RuCl_2$(bmim)], [(η^6-*p*-cymene)RuCl(bmim)(pta)]Cl was isolated in solid form and analogous complexes have been synthesized, too [102].

In aqueous solution, [(η^6-*p*-cymene)$RuCl_2$(bmim)] reacts with (pta-Me)OTf or *m*tppms-Na in a similar way to its reaction with pta. The resulting complexes take part as active catalysts in redox isomerization of allylic alcohols, both in a hydrogen atmosphere and in the presence of HCOONa or other formate salts. In general, no saturated alcohols are formed in the presence of formates. Table 3.2.3 displays the results obtained in isomerization of 1-octen-3-ol, however, other allylic alcohols of the composition H_2C=CH-CH(OH)-$(CH_2)_n$-CH_3 (n = 1–3) reacted with similar conversions and selectivities [101].

The data in Table 3.2.3 show results of the experiments at pH = 7, where conversions were at maximum. It should be born in mind, however, that changes in the pH of the catalyst-containing aqueous phase influenced both the conversion and selectivity between the isomerized and hydrogenated products [101].

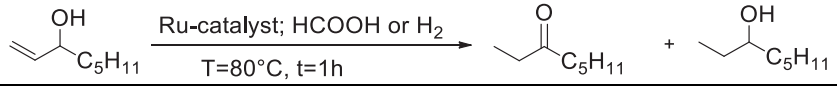
3.3. Hydration of nitriles with phosphaurotropine-containing Ru(II)-complex catalysts

Catalytic hydrations represent a group of reactions where water primarily serves as one of the reagents, but it may also play the role of the solvent, which offers environmental benefits. Selective hydration of nitriles and alkynes are most useful synthetic reactions, however, classical procedures usually employ acids or bases



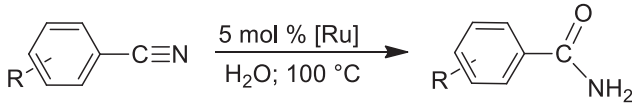
Scheme 3.2.6. Reactions of [(η⁶-*p*-cymene)$RuCl_2$(bmim)] and pta in aqueous solution.

Table 3.2.3
Redox isomerization of 1-octen-3-ol catalyzed by various (η⁶-*p*-cymene)Ru(II)–NHC complexes with water-soluble phosphine ligands



Catalyst	Yield (%)		
	H_2[a]		HCOONa[b]
	octan-3-one	octan-3-ol	octan-3-one
[(η⁶-*p*-cymene)$RuCl_2$(bmim)]	81	9	97
[(η⁶-*p*-cymene)RuCl(bmim)(pta)]	91	5	100
[(η⁶-*p*-cymene)RuCl(bmim)(pta-Bn)]Cl	96	4	83
[(η⁶-*p*-cymene)RuCl(bmim)(*m*tppms)]*	90	0	100

Reaction conditions: n(substrate) = 1 mmol, n(Ru) = 0.01 mmol; [a]3 mL 0.1 M aq. phosphate buffer, pH = 7, p(H_2) = 1 bar, ill. *Ar; [b]3 mL 0.1 M HCOONa.



Scheme 3.3.1. Catalytic hydration of benzonitriles.

as catalysts or as auxiliaries, which may exclude the use of acid- or base-sensitive substrates and produces unwanted salts as byproducts. Specifically, hydration of nitriles leads to amides as the first products, which, however, may be further hydrolyzed to acids. Complexes of Ru(II) are among the most active and selective of such catalysts [103–104]. Examples of nitrile hydrations in neutral aqueous media catalyzed by Ru(II) complexes containing pta or derivatives are discussed in this section.

3.3.1. Phosphaurotropine-containing (arene)Ru(II)- or (dmso)Ru(II)-complexes as catalysts

Cadierno, Gimeno and co-workers successfully applied a number of [(η⁶-arene)$RuCl_2$(P)] P = PPh_2CH_2NHR (R=^{i}Pr, ^{t}Bu), $P(NMe_2)_3$, *tris*-(5-(2-aminothiazolyl)phosphine) half-sandwich complexes for hydration of nitriles in aqueous media [103–104]. Complexes with P = pta, (pta-Bn)Cl, dapta (3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane), and *m*tppms-Na ligands were also included in these investigations [56].

The hydration reactions were carried out usually with 5 mol% catalyst at reflux temperature (Scheme 3.3.1).

With the use of [(η⁶-arene)$RuCl_2$(P)] complexes containing pta or its derivatives, 1 mmol benzonitrile yielded benzamide with 98% conversion in 2–9 h, while such high conversion could not be achieved even in 48 h with the catalyst containing monosulfonated triphenylphosphine (P = *m*tppms). It was suspected, that the nitrogen atoms of pta facilitated the activation of H_2O via hydrogen bonding.

The efficiency of [(η⁶-arene)$RuCl_2$(pta)] catalysts is significantly influenced by its arene ligand: arene = C_6Me_6: TOF = 5.0 h^{-1}; 1,3,5-$C_6H_3Me_3$: TOF = 4.0 h^{-1}; *p*-cymene: TOF = 2.2 h^{-1}; benzene: TOF = 2.0 h^{-1} [56]; toluene: TOF = 1.3 h^{-1} [105]. The catalytic activity of [(η⁶-arene)$RuCl_2$(pta-Bn)]Cl complexes varied in the same order as a function of the arene ligand, however, these catalysts were twice as active as their pta-containing counterparts [56].

Upon the action of the most efficient [(η⁶-C_6Me_6)$RuCl_2$(pta-Bn)]Cl catalyst, several aromatic and aliphatic nitriles were completely hydrated in less than 5 h (in some instances in 1–2 h) reaction times. The catalyst tolerated a number of functional groups such as halide, nitro, hydroxy, ether, thioether, amino, ketone, aldehyde, ester, and alkyne substituents on the aromatic ring. Hydration of acrylonitrile presents a special challenge, since in addition to the hydration of the nitrile group, C = C hydration and polymerization of the subtrate acrylonitrile and the product acrylamide can all happen. Gratifyingly, with [(η⁶-C_6Me_6)$RuCl_2$(pta-Bn)]Cl as the catalyst, completely selective hydration of acrylonitrile to acrylamide was observed. After purification of the product with the use of column chromatography, acrylamide was isolated in analytical purity with up to 91% yield. This process constitutes an outstandingly successful example of production of an industrially important chemical by homogeneous catalytic hydration [56].

Replacement of conventional heating by microwave irradiation led to substantial increase of the conversions in benzonitrile hydrations. With MW irradiation, the reaction temperature could be set to 150 °C (instead of the approximately 100 °C at reflux), and under such conditions the use of 5 mol% [(η⁶*p*-cymene)$RuCl_2$(pta)] led to a turnover frequency of TOF = 76.8 h^{-1} instead of the TOF = 9.9 h^{-1} found at reflux temperature. The [(η⁶-*p*-cymene)$RuCl_2$(pta)] catalyst was also applied in heterogenized form (nanoRAPTA;

Table 3.3.1
Hydration of various nitriles to amides catalyzed by [(η^6-*p*-cymene)$RuCl_2$(pta-Bn)]Cl and the catalysts formed in situ in the reaction of a) [{(η^6-*p*-cymene)$RuCl_2$}$_2$] and 6 eq. (pta-Bn)Cl; b) [$RuCl_2(dmso)_4$] and 3 eq. (pta-Bn)Cl [106].

Entry	Substrate	Conversion[a], % {Yield[b],%}		
		[(η^6-*p*-cymene)$RuCl_2$P] P = (pta-Bn)Cl [Ru]:[P] = 1 : 1	[(η^6-*p*-cymene)$RuCl_2$]$_2$ + 6 (pta-Bn)Cl [Ru]:[P] = 1 : 3	[$RuCl_2(dmso)_4$] + 3 (pta-Bn)Cl [Ru]:[P] = 1 : 3
1	Benzonitrile	23	99 {38}	99 {42}
2	4-Tolunitrile	25	98 {49}	99 {64}
3	4-Chlorophenyl-acetonitrile	43	96 {51}	98 {56}
4	4-Chlorobenzonitrile	98	98 {60}	98 {59}
5	4-(Trifluoromethyl)benzonitrile	89	90 {43}	95 {47}
6	3-Phenylpropionitrile	26	98 {27}	97 {16}
7	1,3-Dicyanobenzene	99	99 {99}	99 {91}
8	1,4-Dicyanobenzene	99	99 {99}	99 {99}
9	4-Nitrobenzonitrile	99	98 {49}	98 {77}
10	3-Pyridinecarbonitrile[c]	96	95	99
11	4-Pyridinecarbonitrile[c]	99	97	99
12	2-Pyridinecarbonitrile[c]	0	20	10
13	Propionitrile[c]	13	85	95
14	Butyronitrile[c]	7	82	92
15	i-Butyronitrile[c]	10	92	97
16	Acetonitrile	0	0	0

Reaction conditions: 5 mol% Ru, 1 mmol substrate, 3 mL water, reflux, 1 h, [a]determined by GC; [b]Isolated product (by decantation) in braces; [c]No solid product separated.

Scheme 3.2.4), on the surface of silica-coated ferrite nanoparticles. Interestingly, the catalytic activities of the homogeneous and heterogenized catalysts were unexpectedly close: 1 mmol of benzonitrile was hydrated to benzamide with 99% conversion in 80 min by the homogeneous, and in 90 min by the heterogenized [(η^6-*p*-cymene)$RuCl_2$(pta)] catalysts. Heterogenization of the pta-containing catalyst on a magnetic support allowed its easy separation from the aqueous reaction mixture with no need for extraction with an organic solvent [92].

The catalytic activity of the [(η^6-*p*-cymene)$RuCl_2$(P)] (P = pta, or pta-Bn) complexes can be increased also by providing a ligand excess. For example, with the use of [(η^6-*p*-cymene)$RuCl_2$(pta-Bn)]Cl alone, 23% benzamide was obtained in 1 h, however, addition of 1 equivalent of [(pta-Bn)]Cl increased the conversion to 89%, which was further increased to 98% in the presence of 2 eq. ligand excess. Surprisingly, the catalysts obtained in situ from [{(η^6-*p*-cymene)$RuCl_2$}$_2$] and (pta-Bn)]Cl were even more efficient. At a [P]/[Ru] = 1 ratio, conversion of benzonitrile was 65% in 1 h, this increased to 95% at [P]/[Ru] = 2, while addition of another eq. pta-Bn led to an almost complete reaction (99% conversion at [P]/[Ru] = 3) [106].

From the data of Table 3.3.1 it may be concluded, that in most cases the in situ prepared catalyst was more active also with substituted benzonitrile substrates, and the same holds for aliphatic nitriles, too. Some of the amide products crystallized out from the reaction mixture at 0 °C in analytical purity (yields of these crystalline products are shown in braces). Incomplete crystallization or partial dissolution of the product, though, may prevent its complete collection, and in such cases, extraction with suitable solvents can result in higher isolated yields [106].

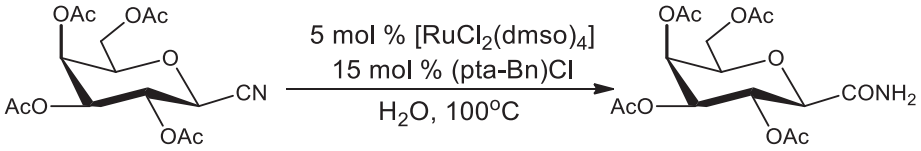
cis-[$RuCl_2(dmso)_4$] was found inactive in benzonitrile hydration, and the same was observed with its mixtures with *m*tppms-Na (up to [P]/[Ru] = 3). In the presence of *cis*,*cis*,*trans*-[$RuCl_2(dmso)_2$(pta-Bn)$_2$]Cl_2, 15% benzamide was obtained in 1 h, and 34% in 2 h reaction time. For comparison, *cis*,*cis*,*trans*-[$RuCl_2(dmso)_2(pta)_2$] required 2 h to produce 13% benzamide. The catalysts, prepared in situ from *cis*-[$RuCl_2(dmso)_4$] and 3 eq. pta, or (pta-Bn)Cl, showed considerably higher activities: with pta, as the ligand, 45% of benzonitrile was converted to benzamide in 1 h, while with N-benzyl-pta, 99% of this substrate reacted (Table 3.3.1). In both cases, 2-pyridinecarbonitrile reacted sluggishly (entry 12), and acetonitrile did not undergo hydration at all (entry 16). Both nitriles are known to coordinate strongly to Ru(II) which could lead to low or nil reactivity. Table 3.3.1 shows, that for all substrates the activity of the in situ prepared half-sandwich complexes lagged behind the efficiency of Ru(II)-dmso-based catalysts. Aqueous solutions containing [$RuCl_2(dmso)_4$] and 3 eq. (pta-Bn)Cl were found suitable for recycling. For example, even at the end of the 6th cycle, benzonitrile was hydrated with 95% conversion (GC yield) [106].

The catalyst prepared in situ from [$RuCl_2(dmso)_4$] and 3 eq. (pta-Bn)Cl was successfully applied for hydration of glucosyl cyanides. As an example, *O*-peracetylated β-D- galactopyranosyl cyanide was hydrated to the corresponding *C*-galactosyl formamide with 85% isolated yield.

Conditions of the procedure (shown on Scheme 3.3.2) were suitable for the catalytic hydration of *O*-benzyl and *O*-benzoyl-protected substrates, too, which all gave the respective *C*-galactosyl formamides with good to high yields [107].

3.3.2. Hydration of nitriles catalyzed by trans-[$RuCl_2(pta)_4$], and the catalysts generated in situ in aqueous solutions of $RuCl_3$ and pta

Hydration of nitriles with *trans*-[$RuCl_2(pta)_4$] as the catalyst was first studied by Frost and Lee. Under conditions of Scheme 3.3.1, on air, benzonitrile was almost completely (99%) converted to benzamide in 7 h. Aqueous solutions of the catalyst remained stable for weeks, and could be recycled at least for five times without the loss of activity. With a concentration of catalyst as low as 0.001 mol% (instead of the usual 5 mol%) an impressive TON = 17000 was



Scheme 3.3.2. Hydration of β-D-galactopyranosyl cyanide to *C*-galactosyl formamide with an in situ prepared [$RuCl_2(dmso)_4$] + 3 (pta-Bn)Cl catalyst [107].

Table 3.3.2
Substrate scope of nitrile hydration catalyzed by *trans*-[$RuCl_2(pta)_4$] [108] or in situ generated catalyst ($RuCl_3$ + 6 eq. pta) [109].

Entry	Substrate	Conversion[a], % {Yield, %}		
		[$RuCl_2(pta)_4$] H_2O	$RuCl_3$ + 6 eq. pta H_2O	$RuCl_3$ + 6 eq. Pta pH 6.8 buffer
1	Benzonitrile	99 {91}[b]	99 {93}[b]	99 {91}[b]
2	2-Tolunitrile	83 {67}[c]	87 {94}[b]	99 {67}[c]
3	3-Tolunitrile	96 {84}[b]	98 {83}[b]	99 {71}[b]
4	4-Tolunitrile	97 {77}[c]	98 {82}[c]	99 {68}[c]
5	4-Methoxybenzonitrile	90 {78}[c]	86 {85}[b]	99 {80}[c]
6	4-Hydroxybenzonitrile	89 {90}[c]	32 {91}[b]	99 {94}[b]
7	4-Nitrobenzonitrile	99 {86}[b]	98 {85}[b]	99 {89}[b]
8	4-Bromobenzonitrile	99 {73}[c]	34 {69}[c]	99 {80}[c]
9	4-Cyanobenzaldehyde	99 {87}[b]	–	–
10	2-Pyridinecarbonitrile	43 {72}[b]	11{49}[b*]	16 {29}[b*]
11	4-Methylbenzyl cyanide	99 {81}[c]	–	–
12	Heptyl cyanide	72 {88}[b]	13{69}[b*]	78 {87}[b*]
13	Trimethylacetonitrile	67 {85}[b]	–	–
14	Acetonitrile	99 {87}[b]	–	–

Reaction conditions: nitrile (1 mmol), water (3 mL) or buffer (3 mL), in air at 100 °C; *trans*-[$RuCl_2(pta)_4$] (0.05 mmol) or $RuCl_3{\cdot}3H_2O$ (0.05 mmol) and pta (0.3 mmol); [a]Conversion determined by GC–MS after 7 h; [b]Isolated by column chromatography after 7 h; [b*]Isolated by column chromatography after 24 h; [c]Isolated by decantation after 7 h.

Table 3.3.3
Hydration of benzonitrile catalyzed by various Ru(II)-pta complexes ([42]).

Entry	Catalyst	Conversion* (%)		
		1 h	2 h	3 h
1	*trans*-[$RuCl_2(pta)_4$] (**1**)	32	65	80
2	*trans*-[$RuCl_2(pta)_4$] + 1 eq. (pta-Bn)Cl	94	95	98
3	*mer,trans*-[$RuCl_2(H_2O)(pta)_3$] (**18**)	29	65	80
4	*mer,trans*-[$RuCl_2(H_2O)(pta)_3$] + 1 eq. pta	43	91	99
5	*mer,trans*-[$RuCl_2(H_2O)(pta)_3$] + 1 eq. (pta-Bn)Cl	90	94	98
6	[{$Ru(pta)_3$}$_2$(μ-Cl)$_3$]Cl (**21**Cl)	81	84	89
7	*cis*-[$RuCl_2(pta)_4$] (**2**) + *cis*-[$RuCl(H_2O)(pta)_4$]$^+$ (**6**)	3	13	29
8	*cis*-[$RuCl_2(pta)_4$] (**2**) (+5 eq. NaCl)	14	47	64
9	*trans*-[$RuCl_2(pta)_4$] (**1**) (+5 eq. NaCl)	17	41	87

Reaction conditions: $n_{benzonitrile}$ = 1 mmol, 5 mol% Ru, V_{H2O} = 3 mL, T = 100 °C, t = 1 h, *GC analysis.

determined [108]. Reaction of substituted benzonitriles and aliphatic nitriles also proceeded with good yields of the corresponding amides (Table 3.3.2).

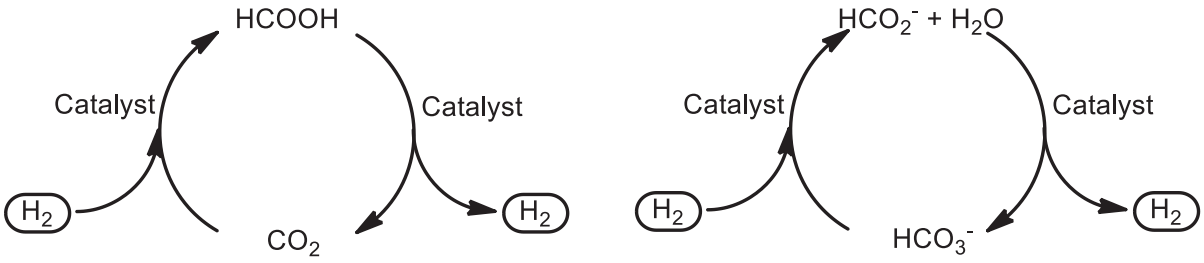
Reaction mixtures of benzonitrile hydrations were studied by NMR spectroscopy. Based on the appearance of signals of free pta and coordinated benzonitrile, formation of $[Ru(pta)_x(H_2O)_y(PhCN)_{6-x-y}]^{2+}$ species was suggested [108]. The role of a putative aquo-species may be supported by that the activity of *mer,trans*-[$RuCl_2(H_2O)(pta)_3$] (**18**) was found higher than that of *trans*-[$RuCl_2(pta)_4$] (**1**) (Table 3.3.3 Entry 1 and 3). Nevertheless, it should be born in mind, that **18** can convert to a dinuclear species at > 80 °C. Note, that [{$Ru(pta)_3$}$_2$(μ-Cl)$_3$]Cl proved to be the most active in the first hour of nitrile hydration (Table 3.3.3 Entry 5), however, its nuclearity under the actual reaction conditions was not established [42].

Irradiation of aqueous solutions of *trans*-[$RuCl_2(pta)_4$] (**1**) results in formation of *cis*-[$RuCl_2(pta)_4$] (**2**) and *cis*-[$RuCl(H_2O)(pta)_4$]$^+$ (**6**) approximately in a ratio of 1:3. This is manifested in a significant decrease of the catalytic hydrogenation of benzonitrile (Table 3.3.3 Entry 1 and 7). In the presence of excess chloride (at least 5 equivalents), the exclusive species in the solutions was *cis*-[$RuCl_2(pta)_4$] and the activity approached that of *trans*-[$RuCl_2(pta)_4$] + 5 eq. chloride (Table 3.3.3 Entry 8–9). Similar to the findings discussed in section 3.3.1, presence of an excess of phosphine (especially that of (pta-Bn)Cl) increased the degree of conversions (Table 3.3.3 Entry 1–2) [42].

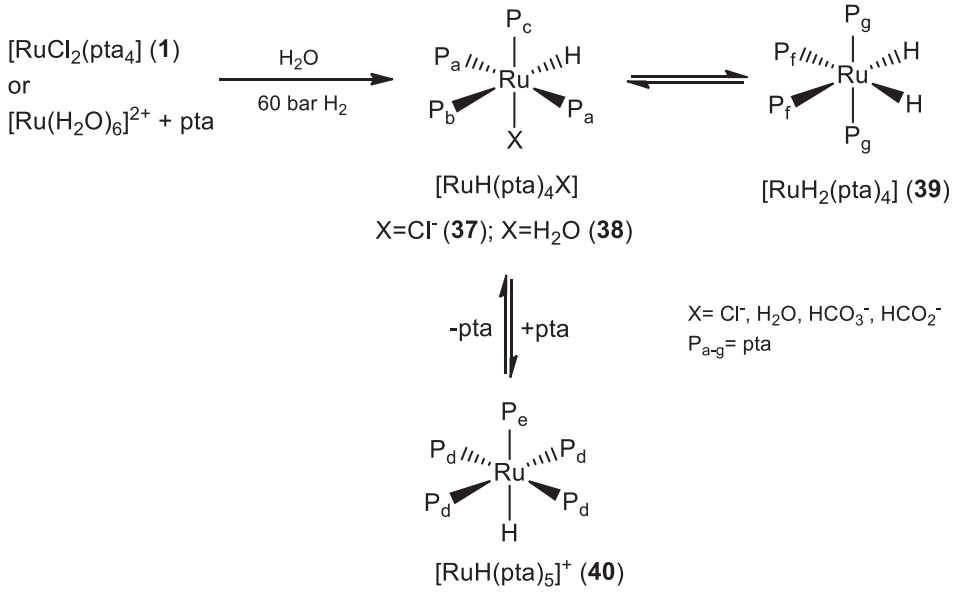
Frost and co-workers studied in detail the catalytic activity of mixtures with [pta]/[$RuCl_3$] = 6 both in water and in aqueous phosphate buffer of pH = 6.8. In the buffered solutions the conversions were systematically higher than in water (TOF = 0.4–6.6 h^{-1} vs. TOF = 0.5–2.8 h^{-1}, respectively) (Table 3.3.2) [109]. Similarly, the isolated [$RuCl_2(pta)_4$] also showed higher activity in buffer: hydration of benzonitrile was characterized by a TOF = 134.5 h^{-1} in buffer vs. TOF = 39 h^{-1} in water. Although the turnover frequencies were largely different, it was concluded, that the actual catalytic species could be similar (if not identical) in the two systems, however, in situ generation of the catalyst needed more time, manifested as an induction period in the experiments.

In case of the benzonitriles with electron donating substituents, somewhat lower conversions were achieved than with similar substrates having electron withdrawing substituents. Aliphatic nitriles were found less reactive, however, the industrially important acrylonitrile was fully converted to acrylamide in 7 h without polymerization of the substrate or the product. The in situ prepared catalyst could be reused at least 7 times with no loss of activity, (similar to the case of *trans*-[$RuCl_2(pta)_4$]) [109].

In summary, it can be concluded, that the in situ generated catalysts show all the beneficial properties of isolated *trans*-[$RuCl_2(pta)_4$]: they are air stable, recyclable, and catalyze the hydration of a wide array of nitriles selectively to amides. In addition, their use is convenient, since the Ru precursors, available



Scheme 3.4.1. Hydrogen storage and delivery cycles based on hydrogenation of carbon dioxide/bicarbonate and dehydrogenation of formic acid/aqueous formate, respectively.



Scheme 3.4.2. Ru(II)-hydrido complexes formed in the reaction of $[RuCl_2(pta)_4]$ (or $[Ru(H_2O)_6]^{2+}$ + pta) in aqueous solution. (Adapted with permission from G. Laurenczy, F. Joó, L. Nádasdi, *Inorg. Chem. 39* (2000) 5083–5088. Copyright (2000) American Chemical Society).

commercially, need not be converted to well defined complexes prior to catalysis.

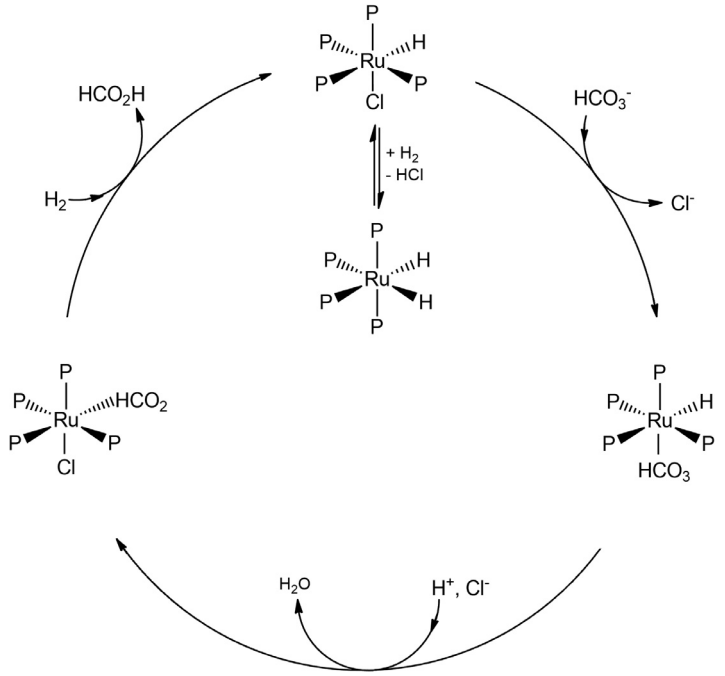
3.4. Hydrogenation of carbon dioxide and bicarbonate

3.4.1. Hydrogenation of CO_2/HCO_3^- With Ru(II)-pta-halide complex catalysts

The concentration of CO_2 in the atmosphere continuously increases bringing about environmental problems due to the greenhouse effect of this gas. On the other hand, CO_2 can be viewed as a C1 building block, however, its activation poses enormous difficulties. Several attempts have been (and are being) made to develop active and durable catalysts for hydrogenation of CO_2 to formic acid, or –in the presence of bases– into formate [110–112]. Most of these studies concerned applications of transition metals other than ruthenium [113–114], and pta was used only sparingly as ligand of the catalytically active complexes. Here we summarize only those results which were obtained with the use of Ru(II)-pta complexes as the catalysts.

Obviously, in aqueous solutions, the formic acid/formate equilibrium is governed by the pH. Formic acid, or aqueous formate solutions may yield H_2 gas upon the action of suitable catalysts, therefore these compounds can be regarded as vehicles for safe chemical storage and transportation of the flammable, explosive gaseous hydrogen [115–120]. Coupling the hydrogenation of CO_2/HCO_3^- to liberation of H_2 gas from the reduced products, HCO_2H/HCO_2^- (preferably with the same catalyst in the two processes) allows construction of a hydrogen storage/delivery cycle or hydrogen battery (Scheme 3.4.1) [121–123]. Apparently, long term applications like hydrogen storage and delivery require extremely stable catalysts, preferably made from easily available, cheap components in most simple procedures.

In the reaction of dimethylamine, supercritical CO_2, and H_2, Jessop and co-workers obtained dimethylformamide with a turnover frequency of TOF = 7200 h^{-1} using $[RuCl_2(PMe_3)_4]$ as the catalyst [110,111] (note that the CO_2 served both as substrate and solvent). Considering the apparent similarity of pta and PMe_3, Laurenczy, Joó and Nádasdi attempted hydrogenation of CO_2 in aqueous solution with *trans*-$[RuCl_2(pta)_4]$ (**1**) as the catalyst [76,124]. Complex **1** reacted only slowly with atmospheric H_2, however, under 60 bar of hydrogen, its originally yellow solution turned almost colourless, and –depending on the solution pH– various Ru(II)-hydrides formed. In acidic solutions $[RuHCl(pta)_4]$ (**37**) and $[RuH(H_2O)(pta)_4]^+$ (**38**) were detected, while in solutions of pH = 12 *cis*-$[RuH_2(pta)_4]$ (**39**) was observed (Scheme 3.4.2). In a later study, a methanolic solution of *trans*-$[RuCl_2(pta)_4]$ (**1**) and HCOONa afforded single crystals of **39**, suitable for structure determination by SC-XRD [33]. While the reaction of **1** with Na-formate furnished **39** with 62% isolated yield, reduction of **1** with H_2 was sluggish, and resulted in only 5% conversion of *trans*-$[RuCl_2(pta)_4]$ to Ru(II)-hydrides (with pH-dependent composition, see above) even under 80 bar H_2. Similarly, **37**–**39** were present in aqueous solu-



Scheme 3.4.3. Suggested reaction mechanism of bicarbonate hydrogenation in aqueous solutions with $[RuCl_2(pta)_4]$ catalyst.

tions of $[Ru(H_2O)_6](tos)_2$ and pta under H_2, but under such conditions, $[RuH(pta)_5]^+$ (**40**) was also formed, due to the low steric demand of pta.

Pressurizing an aqueous solution of *trans*-$[RuCl_2(pta)_4]$ (**1**) at 298 K with a mixture of 20 bar CO_2 and 60 bar H_2 led to formation of formic acid with low efficiency (TOF = 0.24 h^{-1}). At elevated temperature and hydrogen pressure (T = 323 K, $P(H_2) = P(CO_2)$ = 60-bar) the turnover frequency increased to 1.81 h^{-1}. Note, that these reaction mixtures contained no amines or other basic additives. However, when the pH was adjusted with addition of NaOH to 8.7 (when most of CO_2 was present as bicarbonate) a substantial increase in the reaction rate was observed, and formate was obtained with a TOF = 24.5 h^{-1}. Based on medium-pressure NMR measurements it was established, that under actual reaction conditions the most probable catalytic species was $[RuHCl(pta)_4]$] [76]. Scheme 3.4.3 depicts a plausible mechanism of the reaction.

The suggested reaction mechanism involves replacement of the chloride ligand by HCO_3^- resulting in formation of $[RuH(HCO_3)(pta)_4]$. Attempts to detect this (hydrido)(bicarbonato)Ru(II) intermediate with NMR spectroscopy remained unsuccessful. However, in a closely related study on CO_2 and HCO_3^- hydrogenation with $[RuCl_2(pta)([9]aneS_3)]$ ([9]aneS$_3$ = 1,4,7-trithiacyclononane) as the catalyst, $[RuH(HCO_3)(pta)([9]aneS_3)]$ was unambiguously characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy [125]. See also Table 3.4.1) Internal rearrangement of $[RuH(HCO_3)(pta)_4]$, protonation and chloride coordination would afford the Ru(II)-formato intermediate, $[RuCl(pta)_4)(HCO_2)]$. Reaction of this intermediate with H_2 and simultaneous coordination of chloride, regenerates the catalytically active species, $[RuHCl(pta)_4)]$. At the time of their publication, these results represented the highest reaction rates for hydrogenation of CO_2 and HCO_3^- without an organic compound (usually an amine) as a necessary additive.

However, in order to construct a viable cyclic process for chemical hydrogen storage and delivery based on hydrogenation of CO_2 or HCO_3^-, two important problems had to be solved. Bicarbonate hydrogenation could be made fast enough, especially at elevated temperatures and H_2 pressure, but yielded an aqueous solution of Na-formate (or an other formate salt). For a similarly fast hydrogen delivery, efficient catalysts for the reverse reaction, that is for dehydrogenation of aqueous formate are required. Indeed, a few impressive reports have been published on catalytic generation of H_2 from aqueous formate solutions [121–123], however, this method of H_2 delivery has not been widely studied. Furthermore, the catalysts applied for such purposes did not involve Ru(II)-pta complexes, therefore these investigations are not treated in detail here.

On the other hand, catalytic decomposition of formic acid (FA) to yield a H_2 + CO_2 mixture has been in the focus of intensive recent research which resulted in discoveries of catalysts with extremely high activities [114,118–119,126]. However, as mentioned before, in acidic solutions catalytic hydrogenation of CO_2 was too low and incomplete for practical utilization of the process for producing formic acid. Up till now, efforts to use homogeneous catalysts for this purpose have been met with only moderate success and this has remained the main obstacle to develop hydrogen batteries based on the $CO_2 + H_2 \rightleftharpoons HCO_2H$ reversible reaction. Interestingly, though, Ru(II)-pta complexes were found suitable for direct hydrogenation of CO_2 to formic acid in aqueous solutions.

As mentioned earlier, $[RuCl_2(pta)_4]$ catalyzed the hydrogenation of CO_2 in aqueous solutions with no additives, albeit with low efficiency [76,124]. Moret, Dyson and Laurenczy optimized the conditions of this reaction and found that at 200 bar total pressure, $P(H_2)/P(CO_2)$ = 3, T = 60 °C, concentration of formic acid in the reaction mixture reached 0.204 M (TON = 74; TON=(mol reacted substrate)×(mol catalyst)$^{-1}$). Unfortunately, the rate of CO_2 hydrogenation was inconveniently low, since 24–48 h reaction time was needed to reach a steady state. It should be mentioned here, that in the same study, formic acid concentration as high as 1.93 M was arrived at with $[RuCl_2(pta)_4]$ as the catalyst, when neat dimethyl sulfoxide (dmso) was used as solvent (T = 50 °C, 100 bar total pressure, $P(H_2)/P(CO_2)$ = 1). Although the reactions were slow (usually requiring 120 h reaction time) in this solvent, too, the turnover numbers achieved with the use of $[RuCl_2(pta)_4]$ reached TON = 749 and exceeded approximately 20 times those obtained with other complexes [127].

Table 3.4.1
Hydrogenation of HCO_3^- with half-sandwich Ru(II)-complexes containing water-soluble phosphine ligands [53].

Entry	Ru(II)-catalyst or precursor	P	[P]:[Ru]	TOF_0 (h^{-1})
1	[{(η^6-benzene)$RuCl_2$}$_2$]	pta	1:1	67
2	[{(η^6-benzene)$RuCl_2$}$_2$]	pta	2:1	91
3	[{(η^6-*p*-cymene)$RuCl_2$}$_2$]	*m*tppts-Na_3	2:1	25
4	[{(η^6-*p*-cymene)$RuCl_2$}$_2$]	pta	1:1	120
5	[(η^6-*p*-cymene)$RuCl_2$(pta)]	–	1:1	139
6	[(η^6-*p*-cymene)$RuCl_2$(pta)]	pta	2:1	207
7	[(η^6-*p*-cymene)$RuCl_2$(pta)]	pta	3:1	287
8	*trans*-[$RuCl_2$(pta)$_4$]*	–	4:1	35
9	[$RuCl_2$(pta)(9aneS_3)]**	–	1:1	0.12

Reaction conditions: [Ru] = 2 mM, [HCO_3^-] = 1 M, $P(H_2)$ = 100 bar, T = 70 °C; *T = 50 °C [76]; **[Ru] = 1.2 mM, [HCO_3^-] = 0,15 M, T = 30 °C [125].

3.4.2. Phosphaurotropine-containing (arene)ruthenium(II) complexes as catalysts of CO_2/HCO_3^- Hydrogenation and formic acid dehydrogenation

(η^6-Arene)ruthenium(II) complexes containing pta or its derivatives as ligands were also studied to some extent in hydrogenation/dehydrogenation of CO_2/HCO_2H and HCO_3^-/HCO_2^- couples. Reactions of the areneruthenium(II) complexes with hydrogen were scrutinized also in the absence of carbon dioxide or bicarbonate.

In aqueous solutions, the reactions of [{(η^6-benzene)$RuCl_2$}$_2$] and [{(η^6-*p*-cymene)$RuCl_2$}$_2$] with hydrogen and pta afforded as the main products [(η^6-benzene)RuH(pta)$_2$]$^+$ and [(η^6-*p*-cymene)RuH(pta)$_2$]$^+$ [53]. $NaHCO_3$ was hydrogenated at T = 50–70 °C in D_2O with Ru(II)-catalysts obtained in situ from [{(η^6-arene)$RuCl_2$}$_2$] (arene = benzene, *p*-cymene) and pta; the reactions were followed by ^{13}C NMR spectroscopy. The intensity of the HCO_3^- signal decreased monotonously, together with the increase of the ^{13}C signal belonging to HCO_2^-, however, the characteristic doublet ^{13}C NMR resonance of DCO_2^- also appeared in addition to the singlet resonance of HCO_2^-. This clearly showed, that –similarly to other water-soluble Ru(II)-phosphine complexes [52,128]– these half-sandwich Ru(II)-pta complexes catalyzed the H–D exchange, too. Initial TOF values were calculated from the sum of [HCO_2^-] and [DCO_2^-] concentrations [53].

The catalytic activities of the complexes obtained in situ from various precursors and pta in various [P]:[Ru] ratios are shown by the data in Table 3.4.1. For comparison, results for *m*tppts-Na_3 (trisodium salt of tri(*m*-sulfonatophenyl)phosphine) (entry 3), *trans*-[$RuCl_2$(pta)$_4$] (entry 8), and for the [$RuCl_2$(pta)(9aneS_3)] catalyst (entry 9) are also included.

The half-sandwich complexes with η^6-*p*-cymene ligand showed higher activity than those with η^6-benzene (entries 1 vs 4). Increase of the [P]:[Ru] ratio resulted an increase of the activity (entries 2 vs 3). The catalyst obtained from trisulfonated triphenylphosphine (*m*tppts) and [{(η^6-*p*-cymene)$RuCl_2$}$_2$] was much inferior to the ones with pta as phosphine ligand. Although the different reaction conditions do not allow strict comparisons, it seems that replacement of the arene ligand with the macrocycle, 1,4,7-trithiacyclononane, did not increase the catalytic activity of the Ru(II)-pta catalyst substantially (entries 5 vs 9) [125]. The arene-free *trans*-[$RuCl_2$(pta)$_4$] showed comparable catalytic activity to that of the half-sandwich complexes (considering the different reaction temperatures).

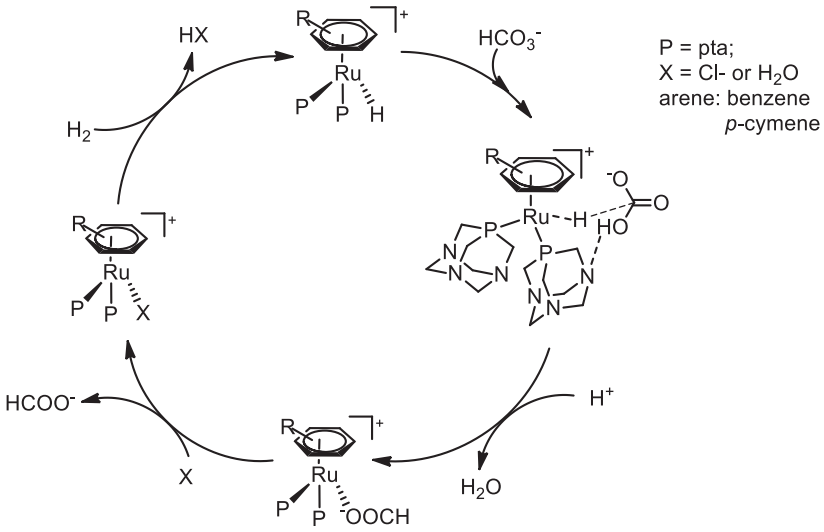
The isolated complex, [(η^6-*p*-cymene)$RuCl_2$(pta)] proved slightly more active as the one formed in situ at [P]:[Ru] = 1 ratio (entries 4 vs 5), moreover, the activity could be further increased by increasing the [P]:[Ru] ratio up to 3 (entries 5–7). Earlier in this review (Section 2.3), we have already discussed that reactions of [(η^6-arene)$RuCl_2$(pta)] with 100 bar H_2 at T = 50–70 °C yielded [(η^6-arene)RuHCl(pta)] and [(η^6-arene)RuH(H_2O)(pta)]$^+$, furthermore, in the presence of excess pta ([P]:[Ru] ≥ 2), [(η^6-arene)RuH(pta)$_2$]$^+$ complexes were also formed. Apparently, the *bis*(pta) Ru(II) complexes have higher catalytic activity in hydrogenation of bicarbonate than those containing only one pta ligand. Although no direct experimental evidence could be collected, it was suggested, that hydrogen bonding between the pta ligand of the catalytically active Ru(II)-complex and the substrate, as shown on Scheme 3.4.4, facilitated the hydrogenation of bicarbonate.

An amine function, linked to the η^6-arene ligand in RAPTA-type Ru(II)-complexes, may help interaction of a catalyst with substrates suitable for hydrogen bonding [53]. To test this hypothesis, Laurenczy and co-workers have synthesized [(η^6-benzyldimethylamine)$RuCl_2$(pta)] the first time. This compound was applied as precatalyst in dehydrogenation of formic acid in the 70–100 °C temperature range. Decomposition of formic acid to H_2 and CO_2 started with pronounced induction periods at all temperatures, but 100% conversions of the substrate could be achieved in all cases; at 100 °C full conversion required approximately 2 h. From the linear parts of the kinetic curves an activation energy (E_a) of 95.59 ± 4 kJ × mol^{-1} was calculated. Addition of 1 equivalent pta to an aqueous solution of [(η^6-benzyldimethylamine)$RuCl_2$(pta)] before addition of formic acid, not only eliminated the induction period but led to much faster reactions, so much that at 100 °C full conversion of the substrate was observed in only 20 min. These results were rationalized by considering formation of [(η^6-benzyldimethylamine)RuH(pta)$_2$]$^+$ (similar to the one shown on Scheme 3.4.4) as the actual catalyst. In accordance with the higher reaction rates, a smaller apparent E_a value (88.67 ± 4 kJ/mol) was determined for the reaction with the supposed *bis*(pta)Ru(II) catalyst than with [(η^6-benzyldimethylamine)$RuCl_2$(pta)] in the absence of added pta [120].

4. Conclusions and outlook

The synthesis of 1,3,5-triaza-7-phosphaadamantane in the very simple reaction of aqueous ammonia, formaldehyde and P(CH_2-OH)$_3$ with no protection from air, gave an unique compound into the chemists' hands. Versatility and usefulness of pta is due to its high water-solubility, oxidation stability, easy functionalization, and the presence of four potential donor atoms for coordination to metal ions.

Apart from its other applications, pta is used in coordination chemistry and catalysis as a tertiary phosphine ligand. This paper deals with Ru(II)-phosphaurotropine complexes, first of all with pta and alkylated pta ligands. A specific point of selection was the simplicity of synthesis of such Ru(II)-pta complexes, either directly from hydrated Ru(III)-halides, or from easy-to-synthesize, well defined, water-soluble Ru(II)-precursors such *cis*-[$RuCl_2$(dmso)$_4$] and [{(η^n-arene)$RuCl$}$_2$(μ-Cl)$_2$] dimers, which are also available commercially. Reactions of these precursors with pta or its derivatives yield a large number of Ru(II)-phosphaurotropine complexes with astonishingly diverse



Scheme 3.4.4. Suggested mechanism of the hydrogenation of bicarbonate with use of half-sandwich Ru(II)-pta catalysts.

properties. Of those, several are able to catalyze important reactions in aqueous media, such as the selective hydrogenation of unsaturated aldehydes, redox isomerization of allylic alcohols, hydration of nitriles and hydrogenation of CO_2/HCO_3^- and dehydrogenation of $HCO_2H/HCO_{2(aq)}^-$. A few important generalizations emerge from studies on formation and catalytic properties of Ru (II)-phosphaurotropine complexes:

- Being a basic and sterically undemanding ligand, pta forms stable complexes with Ru(II). Coordination of several pta ligands often leads to coordinative saturation e.g. in $[RuCl_2(pta)_4]$, or $[RuH(pta)_5]^+$ which are catalytically less active or inactive in certain reactions.
- In aqueous solution, several Ru(II)-pta-halide complexes undergo halide replacement by H_2O. This reaction yields (aquo)Ru(II)-pta species containing an easily exchangeable water ligand. In general, this is advantageous for catalysis.
- With Ru(II) (or with other low-valent transition metal ions) N-coordination of pta is atypical.
- The presence of N-atoms in pta and its derivatives makes these ligands suitable for establishing hydrogen-bonds which results in easy crystallization (or formation of coordination polymers) of Ru(II)-phosphaurotropine complexes.
- Hydrogen bond(s) may form between a Ru(II)-bound-pta and the incoming substrate. Also, pta ligands can act as proton acceptor/donor (proton shuttle) in the mechanism of catalysis. These effects may influence the rate and selectivity of catalytic reactions.
- In water, several Ru(II)-phosphaurotropine complexes have been found photoactive with no need for an auxiliary photosensitizer.

The above findings mostly concern the catalytic properties and applications of Ru(II)-phosphaurotropine complexes and we expect further research on their use in important catalytic reactions in aqueous solutions, aqueous biphasic systems and in heterogenized form. Other possible applications were only touched in this review, however, biological effects (such as those of RAPTA-type complexes) or photoactivity of certain Ru(II)-phosphaurotropine complexes also may prove highly valuable to study. For this reason, synthetic methodologies based on simple and easily available starting materials will certainly retain their significance in the future, too.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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