Hydration of Propargylic Alcohols by Ruthenium Catalysts, with Dominant Anti-Markovnikov Regioselectivity, Formation of α,β-Unsaturated Products and Catalytic Decarbonylation to 1-Alkenes

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Ruthenium catalysts — water-soluble ruthenium sulfophthalocyanine and heterogeneous ruthenium hydroxyapatite complexes — proved to be effective for the hydration of propargylic alcohols in entirely aqueous media. 1-Phenyl-2-propyn-1-ol underwent an unprecedented catalytic hydration-decarbonylation-dehydration reaction, giving rise to styrene and carbon monoxide; 2-propyn-1-ol and 3-butyn-2-ol gave predominantly the products of anti-Markovnikov addition, together with products of hydration-dehydration (α,β-rearrangement) and, to a minor extent, the decarbonylation products, ethene or propene, respectively. Hydrations were also conducted in D_2O, giving indications of the mechanism of the reactions and apparently ruling out the allenylidene route for the α,β-rearrangement.

Introduction

Alkynes are useful intermediates for the synthesis of carbonyl compounds through the well-known metal-catalyzed hydration reaction. Typically, the addition reactions of water to 1-alkynes are catalyzed by a variety of transition metal salts and complexes,[1−7] including $RuCl_3$,[8,9] all of which follow Markovnikov's rule to give ketones. Only very recently[10] has it been reported that the reaction can be regioselectively oriented to the formation of aldehydes (anti-Markovnikov addition) in the presence of catalytic amounts of some ruthenium(II) organometallic derivatives, containing either cyclopentadienyl[11,12] or indenyl[13] moieties, although temperatures of around 100 °C were still required. The accepted mechanism involves the rearrangement of the π-adduct deriving from the conventional interaction with the terminal alkynes at the metal center into a metal-vinylidene intermediate[13] or, alternatively, a hydrido-alkynyl complex,[12] the latter of which has recently been isolated as an intermediate in the activation of propargylic alcohols by [Cp*RuCl(dppe)];[14] both the proposed intermediates are prone to nucleophilic attack by water at the α-carbon atom. Previous results[15] showed the critical role played by the π-alkyne/vinylidene equilibrium in the regioselectivity of the hydration reactions, suggesting that addition of water to the π-adduct might follow Markovnikov's rule, eventually yielding methylketones, whereas addition to the vinylidene intermediate would lead to an acyl complex and, finally, aldehydes. However, only a few examples have reported good selectivity in the aldehyde formation,[11,13] as several alternative reaction pathways, not strictly dealing with conventional hydration, could become dominant. Among them, the catalytic cleavage of the carbon-carbon triple bond is particularly attractive, since it could represent an interesting topic from the synthetic point of view, if high selectivities can be attained in mild experimental conditions. So far, however, alkyne cleavage has also been demonstrated to work effectively in only a few cases.[16,17]

The potential for the use of both ruthenium catalysts and water as reagent prompted our interest in the subject. In the present work we tested the water-soluble ruthenium(II) complex ruthenium sulfophthalocyanine (RuPcS), previously studied by us as an effective catalyst for a variety of organic substrates in aqueous media,[18−22] and the heterogeneous ruthenium hydroxyapatite (RuHAP) catalyst, successfully tested for the aerobic oxidation of alcohols to aldehydes, reportedly via a metal-hydrido species,[23] which proved to work satisfactorily also in aqueous media.[24] This paper deals with the catalytic hydration of a number of propargylic (2-propyn-1-ol, 3-butyn-2-ol, 1-phenyl-2-propyn-1-ol and 1,1-diphenyl-2-propyn-1-ol) and non-propargylic alcohols (3-butyn-1-ol and 4-pentyn-1-ol). A variety of reaction pathways were observed, depending upon the nature of the substrate and the catalyst; among them, cleavage of

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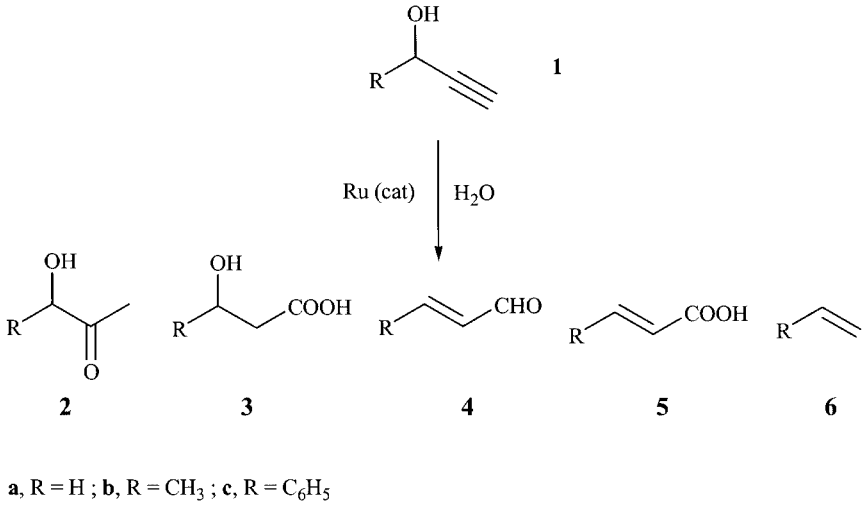


Scheme 1. Product distribution for the hydration of propargylic alcohols catalyzed by Ru^{II} derivatives

the triple bond, with formation of alkenes, was of particular interest (Scheme 1).

Results and Discussion

The RuHAP and RuPcS catalysts proved to be effective, at various selectivities, in the reaction of the terminal acetylenes 1-phenyl-2-propyn-1-ol, 2-propyn-1-ol, 3-butyn-2-ol and 4-pentyn-1-ol with water; no reaction took place in the absence of added catalyst or in the presence of calcium hydroxyapatite, whereas other simple ruthenium complexes, such as $[RuCl_2(DMSO)_4]$ (RuDMS) and $K_5[Ru(H_2O)PW_{11}O_{39}]$ (RuPW), behaved poorly. Very different and complex reaction patterns were found for each substrate examined, as reported in Table 1. The reactions were very slow below 80 °C.

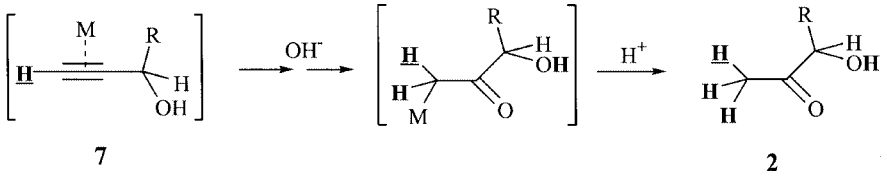
In the presence of RuHAP and RuPcS, the non-propargylic alcohol 4-pentyn-1-ol was selectively transformed into 5-hydroxy-2-pentanone, the expected product of the conventional Markovnikov addition to the triple bond. The related substrate 3-butyn-1-ol (not shown) was poorly converted (about 10 %) during the 24 h reaction time and gave only minor amounts of products from both the Markovnikov and anti-Markovnikov addition, i.e. 4-hydroxy-2-butanone and 4-hydroxybutanoic acid, respectively, together with other unidentified compounds.

The propargylic alcohols behaved differently. Large amounts of 2-propyn-1-ol (**1a**) were converted, in the presence of both RuHAP and RuPcS, into hydroxyacetone (**2a**, the expected product of Markovnikov addition; Scheme 2), 3-hydroxy-propanoic acid (**3a**), acrylic acid (**5a**) and ethene (**6a**), together with minor amounts of glycolic and formic acid (Table 1), the latter likely arising from the oxidative cleavage of the substrate. No evidence was obtained for the presence of 3-hydroxypropanal, which should be the prod-

Table 1. Product analysis of the hydration reaction of propargylic alcohols by ruthenium catalysts[a]

Substrate	Catalyst	Conversion (mol %)	Yields (mol %) 2	3	4	5	6	By-products
1a	RuPcS	73	10	10	–	22	7[b]	8[c]
	RuHAP	70	12	20	–	12	8[b]	5[c]
	RuDMS	9	7	–	–	–	nd	1[c]
	RuPW	8	6	–	–	–	nd	1[c]
1b	RuPcS	70	2	7	–	15	15[b]	5[d]
	RuHAP	65	4	9	–	12	16[b]	5[d]
1c	RuPcS	70	2	–	3	–	16[e]	1[f]
	RuHAP	95	2	–	5	–	20[e]	1[f]
4-Pentyn-1-ol			5-hydroxy-2-pentanone					
	RuPcS	70	69					
	RuHAP	100	99					

[a] Substrate: 400 mM; catalysts: RuPcS, 10 mM; RuHAP, 40 mg/mL (78 mmol of Ru/L); water; 80 °C; 24 h reaction. [b] Measured as their 1,2-dibromo derivatives, after capturing the evolved gases into a bromine solution. [c] Glycolic and formic acid. [d] 2-Propanol. [e] Measured after extraction with diethyl ether; polystyrene and polymeric materials were also detected in not well-defined yields. [f] 1-Phenylethanol.

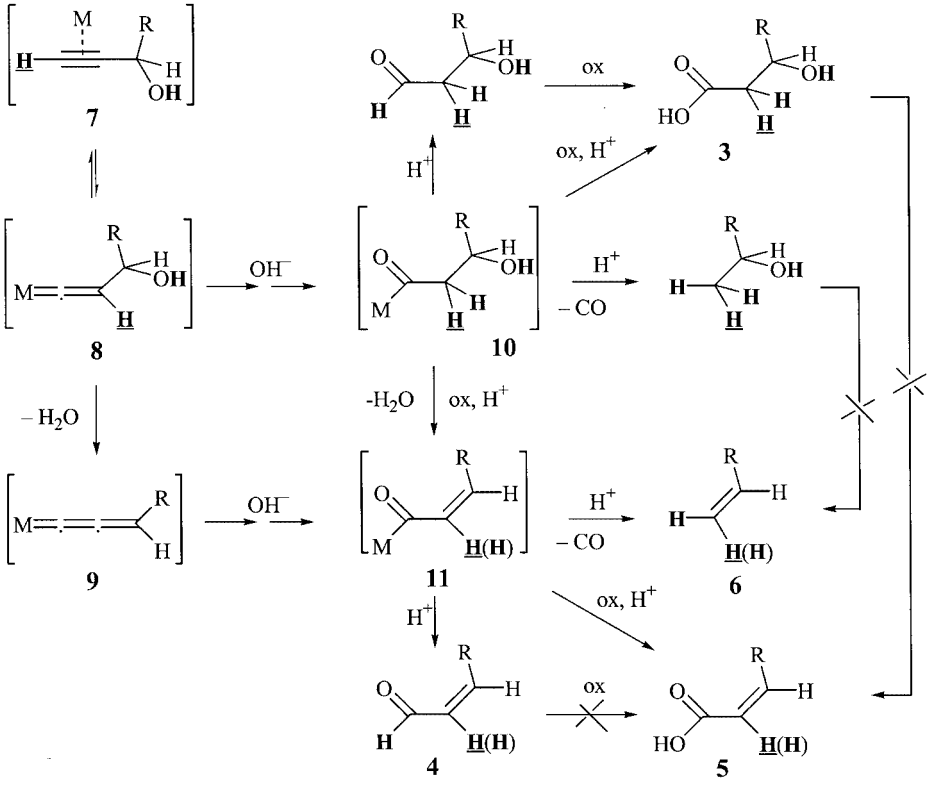


Scheme 2. Ruthenium-catalyzed Markovnikov hydration of propargylic alcohols (**H** coming from water; **H** coming from acetylenic proton)

uct of anti-Markovnikov addition to the triple bond; instead, its oxidized product 3-hydroxy-propanoic acid, was detected in reasonable amounts. To avoid this undesired oxidation, we tried to conduct the reaction under an inert atmosphere (nitrogen), but the long times required for the formation of the products did not allow for a rigorous exclusion of oxygen and, indeed, only minor differences were observed with respect to the aerobic experiments, i.e. with no evidence for the aldehydic product. It should be noted here that aliphatic aldehydes, such as propionaldehyde and valeraldehyde, are easily oxidized to the corresponding carboxylic acids in the same reaction conditions and in the absence of added ruthenium catalysts. The third major reaction product, acrylic acid, could be conceivably attributed to a dehydration of 3-hydroxypropanoic acid. However, experiments conducted directly with β-propiolactone (a commercially available compound that rapidly hydrolyzes to 3-hydroxypropanoic acid in aqueous media) showed only minimal conversion into acrylic acid (less than 5 %) under these standard reaction conditions. The formation of the unsaturated product probably involves the well-known rearrangement of propargylic alcohols to α,β-unsaturated aldehydes, which is effectively catalyzed also by several ruthenium complexes.[25] More recently,[26] Wakatsuki has reported convincing evidence that the mechanism of the ruthenium-catalyzed rearrangement of propargylic alcohols to unsaturated aldehydes involves a series of organometallic intermediates, arising either by an initial anti-Markovnikov hydration of the vinylidene intermediate **8** (Scheme 3), followed by dehydration of the original OH group to **11** via **10**, or, alternatively, by an early dehydration of **8** to an allenylidene intermediate **9**, followed by the hydration step. Thus, the rearrangement of 2-propyn-1-ol was expected to produce acrolein; the observed formation of acrylic acid could again be due to the rapid oxidation of the aldehydic group, as in the case discussed previously. However, acrolein, as other α,β-unsaturated aldehydes, such as benzaldehyde and cinnamaldehyde, and contrary to the saturated aldehydes discussed above, is very difficult to oxidize under these reaction conditions. It is therefore reasonable to assume that acrylic acid is formed directly from the organometallic intermediate **11a** via a complex rearrangement-oxidation step. Finally, we also detected carbon monoxide and an appreciable amount of ethene (**6a**; see Exp. Sect.), which allowed a reasonable mass balance to be set for the overall transformation of **1a**.

The reaction of 3-butyn-2-ol (**1b**) with water closely resembles that of 2-propyn-1-ol and leads to all the expected products from the addition of water according to Markovnikov (hydroxybutanone, **2b**) and anti-Markovnikov rules (hydroxybutanoic acid, **3b**); we also detected the decarbonylated and dehydration/oxidation products, i.e. propene (**6b**) and 2-butenoic acid (**5b**), respectively, and carbon monoxide.

Hydration of 1-phenyl-2-propyn-1-ol (**1c**) reached 70 % and 95 % conversion (with RuPcS or RuHAP, respectively) of the starting material within 24 h (Table 1), but the reaction led to minimal amounts of the product of Markovni-



Scheme 3. Proposed pathway for ruthenium-catalyzed anti-Markovnikov hydration of propargylic alcohols (**H** coming from water; **H** coming from the acetylenic proton)

kov addition [1-hydroxy-1-phenylpropanone (**2c**)] and no conventional products from the anti-Markovnikov addition, i.e. 3-hydroxy-3-phenylpropanal or the corresponding carboxylic acid. In addition, the α,β-unsaturated aldehyde [cinnamaldehyde (**4c**)], arising from the ruthenium-catalyzed rearrangement of the propargylic alcohol, was detected as a minor product. It should be recalled that in the reaction conditions cinnamaldehyde, as with other α,β-unsaturated aldehydes, does not undergo oxidation to the corresponding carboxylic acid and therefore the reported yields must be considered highly significant. Quite unexpectedly, the major product formed during the reaction was styrene (**6c**), which was detected after extraction of the reaction mixtures with diethyl ether (16−20 %; Table 1), together with carbon monoxide and large (but not quantified) amounts of styrene-based polymeric materials, likely accounting for the final mass balance. It should be noted that in the cases of ethene and propene discussed previously, no water-insoluble polymeric materials were detected. However, ethene and propene, unlike styrene, accumulate in the gas phase and therefore are expected to escape from the reaction mixture before they can be polymerised. Therefore the low mass-balance values for both **1a** and **1b** (Table 1) were attributed to some further unidentified products.

No reaction was observed for the other propargylic alcohol, 1,1-diphenyl-2-propyn-1-ol, when suspended in water as it is only slightly soluble. However, when the hydration was carried out in an organic solvent (toluene) with small amounts of added water and in the presence of the lipophilic ruthenium phthalocyanine derivative RuPc, instead of the water-soluble RuPcS, small amounts of 1,1-diphenylethene and of β-phenylcinnamaldehyde were formed, thus indicating a reactivity closely related to that of 1-phenyl-2-propyn-1-ol in the water/RuPcS system.

A simple explanation for the formation of $C_{(n-1)}$ alkenes (styrene, propene and ethene) from the corresponding propargylic alcohols (1-phenyl-2-propyn-1-ol, 3-butyn-2-ol and 2-propyn-1-ol, respectively) might involve decarbonylation of the anti-Markovnikov acyl-metal intermediate **10** to 1-substituted ethanol derivatives followed by a dehydration step (Scheme 3). 2-Propanol and 1-phenylethanol were detected in trace amounts in the case of 1-phenyl-2-propyn-1-ol and 3-butyn-2-ol, respectively. However, the fact that direct experiments conducted in the presence of ethanol, 2-propanol and 1-phenylethanol under the same reaction conditions showed minimal (or no) dehydration to ethene, propene and styrene (less than 2 % in the most favorable case, namely 1-phenylethanol), indicates that the alkenes are formed directly from an organometallic intermediate (likely **11**), in competition with the 1-substituted ethanol derivatives. The formation of alkenes also implies formation of carbon monoxide, which was always detected among the products of the hydration reactions. Decarbonylation of terminal acetylenes by hydration is indeed a known process, first reported by Bruce[27] and thoroughly investigated by Bianchini[28] in the case of phenylacetylene, which, in the presence of water and of the Ru^{II} complex $[RuCl_2(PNP)(PPh_3)]$, was quantitatively transformed into toluene and the stable mono-carbonyl adduct $[RuCl_2(CO)(PNP)]$. Wakatsuki[10] has also reported decarbonylation (likely stoichiometric) during the hydration of benzylacetylene in the presence of 10 % $[RuCl_2(C_6H_6)\{PPh_2(C_6F_5)\}]$. In the present case, decarbonylation turned out to be catalytic, thus indicating lability of the putative carbonylruthenium adducts with either RuHAP or RuPcS. Indeed, RuPcS was previously reported by us[21] to be able to add carbon monoxide, giving a carbonyl product possessing a strong band at 1960 cm^{-1}, but only under very severe conditions (100 atm) and after 24 h reaction.

Hydration Reactions in D_2O

Deuterium distribution in the products was evaluated by ^1H NMR spectroscopy and GC-MS measurements on the reaction mixtures from 2-propyn-1-ol (**1a**) and 1-phenyl-2-propyn-1-ol (**1c**). It has to be noted that acetylenic-proton exchange of the pure substrates in 99.9 % D_2O turned out to be slow even at 80 °C, with 100 % deuteration being reached only after 4 h (Figure 1). The rate of deuterium exchange in the presence of the RuPcS catalyst was similar for 1-phenyl-2-propyn-1-ol, at least at early reaction times, whereas in the case of 2-propyn-1-ol deuteration was much slower and never exceeded 40 % substitution, even after long reaction times (Figure 1). The observed different deuteration rates of the acetylenic proton must be compared with the hydration rates of the corresponding substrates (Figure 1), clearly indicating that 2-propyn-1-ol (**1a**) underwent hydration in D_2O mainly as the protonated RC≡CH

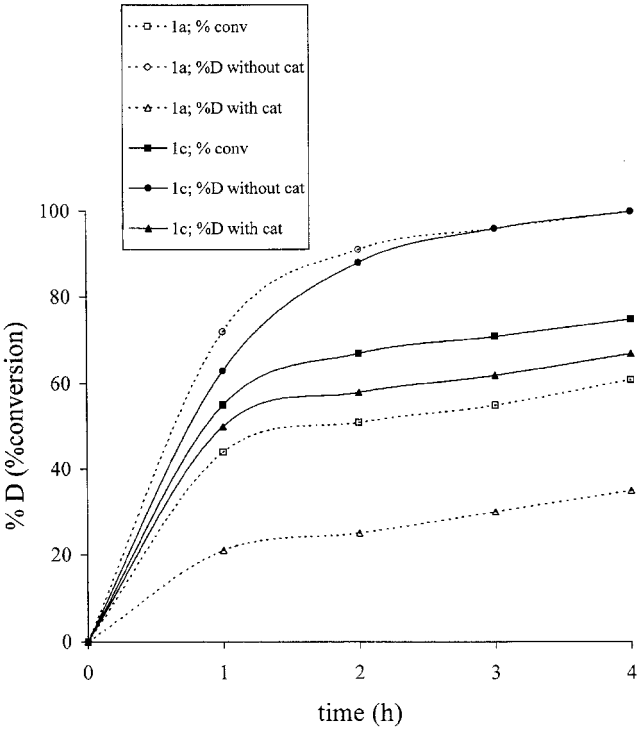


Figure 1. Incorporation of deuterium into 2-propyn-1-ol (**1a**; open squares and triangles, dotted lines) and 1-phenyl-2-propyn-1-ol (**1c**; filled squares and triangles, solid lines); % conversions of **1a** (open circles, dotted line) and **1c** (filled circles, solid line) are also reported

species, while 1-phenyl-2-propyn-1-ol (**1c**) reacts as the deuterated RC≡CD species.

The rapid and almost complete deuteration of the acetylene proton of 1-phenyl-2-propyn-1-ol unfortunately precluded any significant conclusion about the possible mechanism of the hydration of this substrate (Scheme 2 and 3). The ^{1}H NMR spectrum of the product of Markovnikov addition — 1-hydroxy-1-phenylacetone (**2c**) — shows complete disappearance of the singlet arising from the methyl protons, in agreement with the dominant presence of the $CO-CD_3^+$ fragment (46 amu) in the mass spectrum; the molecular ion $CH_3COCH(Ph)OH^+$ is almost undetectable. The ^{1}H NMR spectrum of cinnamaldehyde (**4c**) lacks the signals of the aldehydic proton (doublet) and that of the proton bonded to the α-carbon, whereas the signals of the Ph*C*H=CH−CHO proton are covered by those of the phenyl protons. MS measurements clearly indicated that PhCH=CD−CDO was the dominant species. The ^{1}H NMR spectrum of styrene (**6c**) lacks the multiplets arising from the terminal methylene group, whereas the multiplet of the PhCH= proton collapses into a very broad signal, strongly indicative of an effective coupling with the two deuterium atoms in the α-position; the formula Ph−CH=CD_2 was fully confirmed by the GC-MS data.

Because of the slow deuterium exchange of the acetylenic proton, a selective deuterium distribution in the products was expected for 2-propyn-1-ol. Hydroxyacetone (**2a**, the product of Markovnikov addition) exhibits the $COC\underline{H}H_2$ (see Scheme 2) singlet in the ^{1}H NMR spectra considerably broadened and reduced in intensity, when compared with that of the singlet of the CH_2OH protons, but indicative of ca. 70 % deuteration (Figure 2). The mass spectrum shows the peak of the molecular ion shifted by +3 amu and that of the $COCH_3^+$ fragment by +2 amu (45 instead of 43 amu), in agreement with the dominant presence of the $CD_2H-CO-CH_2OD$ species. The dideuteration of the methyl group in the formed methylketone confirms the slow exchange of the terminal CH, since fast exchange would have yielded trideuteration, as found in 1-hydroxy-1-phenylacetone. The anti-Markovnikov addition of D_2O to RC≡CH probably involves the interconversion of an η^2-alkyne species to a vinylidene, therefore bringing the acetylenic hydrogen onto the carbon substituted with the R group and eventually giving RCHD−CDO (or RCHD−COOD;

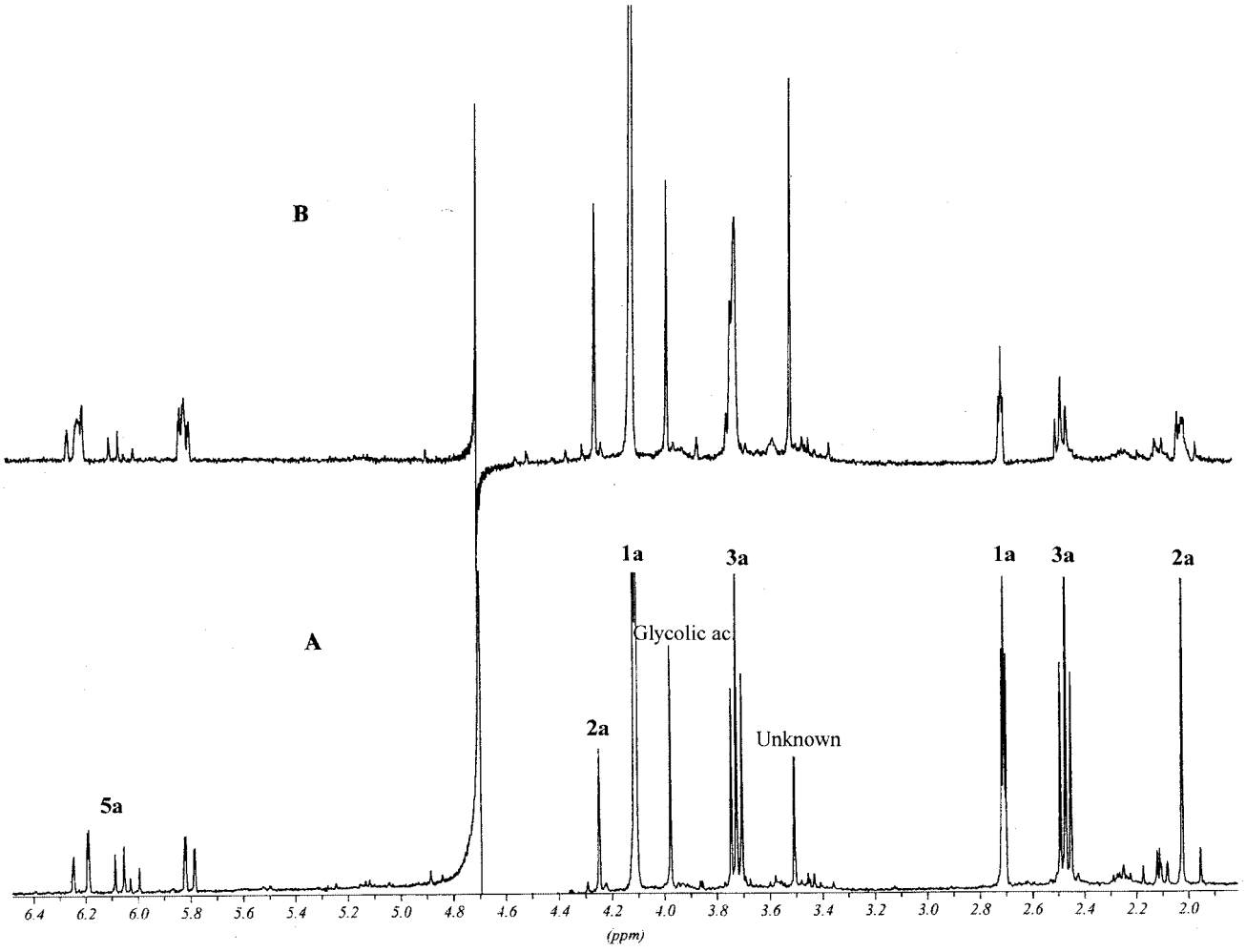


Figure 2. ^{1}H NMR spectra of the crude mixture of the hydration reaction of 2-propyn-1-ol (24 h, 80 °C) in H_2O (**A**) or in D_2O (**B**); the product numbers are the same as in Scheme 1

Scheme 3), unless a rapid proton exchange is taking place on the vinylidene intermediate. We found that 3-hydroxypropanoic acid (**3a**) exhibits a distinctive deuteration at the methylene group next to the carbonyl carbon, with the ^{1}H NMR spectra showing a collapse of the two diagnostic triplets of the CH_2 signals at $\delta = 3.75$ and 2.50 ppm ($J = 6$ Hz) into a broad singlet and a triplet, respectively, in a roughly 2.5:1 intensity ratio (Figure 2) and therefore best fitting with an $HOCH_2-CHD-COOH$ species. No MS measurements were possible, since 3-hydroxypropanoic acid was not detectable in the GC. Acrylic acid (**5a**), arising from the hydration-dehydration reaction, shows the presence of both the $CH_2=CD-COOD$ ($m/z = 73$) and the $CH_2=CH-COOD$ species ($m/z = 72$), roughly in a 1:1 molar ratio. Accordingly, the ^{1}H NMR signals of the hydrogen atom bonded to the carbon atom next to the carboxylic function appear clearly weakened with respect to the signals of the methylene protons (ca. 50 % in intensity; Figure 2). Also ethene (**6a**), the decarbonylation product, exhibits only partial deuteration. The MS spectra of its dibromo adduct CH_2Br-CH_2Br shows an intense fragment arising from the loss of one Br atom as a series of peaks at 108 and 110 amu (^{79}Br) and at 109 and 111 amu (^{81}Br), in an intensity ratio of ca. 1:4, therefore suggesting the presence of both the dideuterated $C_2H_2D_2Br^+$ and monodeuterated $C_2H_3DBr^+$ ions. The latter two findings have some significance, since they apparently rule out the putative allenylidene route (i.e. **8a** → **9a** → **11a**, Scheme 3), for which complete deuteration of the carbon atom next to the metal-acyl function in **11a** was expected, thus eventually yielding exclusively the $CH_2=CD-COOH$ and $CD_2=CH_2$ species; the vinylidene route (i.e. **8a** → **10a** → **11a**, Scheme 3) is not contradictory with the observed formation of partially deuterated products.

Interaction of the Substrates with the Metal Complexes

The nature of the catalyst apparently influences the rate of the hydration more than it does the regioselectivity, which is strongly dependent upon the nature of the substrate. Since an attractive explanation of the observed behavior might be the different degree of stabilization of the π-adduct **7** in Scheme 2 vs. the metal-vinylidene intermediate **8** in Scheme 3, induced by the various substrates, we carefully analyzed an aqueous solution of RuPcS (10 mM) in the presence of increasing amounts of the substrates under investigation, and also, for comparison purposes, of other saturated and unsaturated alcohols (1-butanol, 2-propen-1-ol, ethanol). By increasing the substrate-to-metal ratios up to 20-fold, an enhancement of the measured acidity of the mixtures was generally observed, in some cases very sharp, but always irrespective of the nature of the substrates, and therefore hardly attributable to any significant metal/substrate interaction. Accordingly, ^{1}H NMR measurements of the propargylic alcohols/RuPcS systems in buffered solutions (with pHs varying between 0.5 and 9) exhibited only tiny and erratic shifts of the proton signals

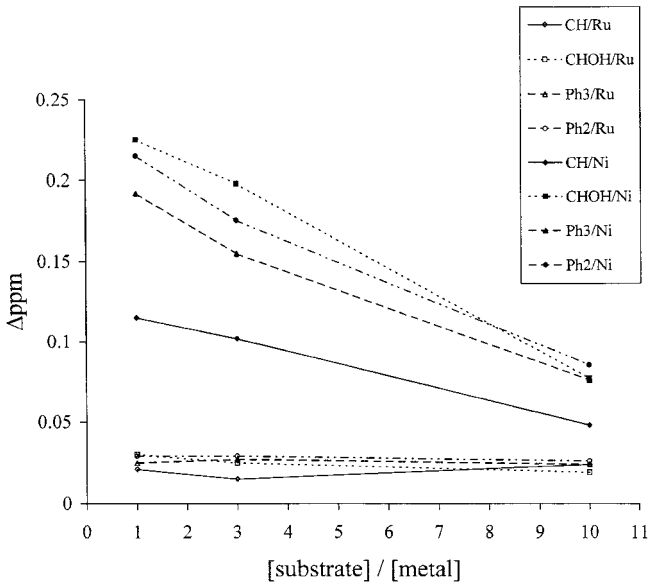


Figure 3. Differences in the ^{1}H NMR chemical shift for 1-phenyl-2-propyn-1-ol in the presence of MPcS's (10 mM), relative to the pure substrate: CH = acetylenic proton; CHOH = aliphatic proton; Ph_2 = *ortho* aromatic protons; Ph_3 = *meta* and *para* aromatic protons.

(±0.01 ppm), including the acetylenic one (Figure 3). For comparison purposes, we investigated other MPcS complexes (M = Fe, Co and Ni), all of them catalytically inactive for the reaction under investigation; for the 1-phenyl-2-propyn-1-ol/NiPcS system significant changes in the ^{1}H NMR spectra were detected by decreasing the substrate-to-metal ratios down to 1 to 1, with pronounced upfield shifts (up to 0.25 ppm) of the aromatic (Ph_2 and Ph_3) and aliphatic (CHOH) protons and less pronounced, but still significant, shifts of the acetylene proton (up to 0.15 ppm; Figure 3). This finding thus strongly suggests a substrate-metal interaction also involving the triple bond.

Conclusion

The first noteworthy finding in this paper is the different reactivity exhibited by the Ru^{II} derivatives in aqueous solution. Simple ruthenium complexes, like RuDMS and RuPW, gave almost exclusively products according to the Markovnikov rule and in very low yields (at least with 2-propyn-1-ol), whereas, when the metal is strongly complexed, i.e. with a phthalocyanine ring or a hydroxyapatite support, the reactivity was definitely enhanced. The regioselectivity was found to be strongly dependent upon the nature of the alkynol; in particular, only when the OH group is relatively close to the triple bond (propargylic alcohols) does the attack of water at the triple bond follow dominantly, if not exclusively, an *anti* Markovnikov pathway (in a broad sense), thus leading to aldehydic (or carboxylic acid) products, α,β-rearrangement of the substrate and/or decarbonylation. The selectivities in each of the above "anti-Markovnikov" products were however moderate and far lower

than those reported with other ruthenium catalysts.[10,13] We have no data to support a real participation of the OH group in the π-adduct/vinylidene species equilibrium, but the fact that definite evidence of a metal−ligand interaction was obtained only for the catalytically inactive NiPcS species, suggests that the driving force of the RuPcS hydrations is essentially kinetic. The other important findings deal with the observed smooth decarbonylation of the propargylic alcohols to corresponding $C_{(n-1)}$ alkenes, which represents, to the best of our knowledge, the first catalytic decarbonylation process of terminal alkynes.

Experimental Section

Materials: Ruthenium tetrasulfophthalocyanine (RuPcS),[21] cobalt tetrasulfophthalocyanine (CoPcS),[29] *cis*-[$RuCl_2(DMSO)_4$] (RuDMS),[30] $K_5[Ru(H_2O)PW_{11}O_{39}]$ (RuPW)[31] and ruthenium hydroxyapatite (RuHAP; Ru 17 %, corresponding to 1.6 mmol/g)[23] were prepared by published procedures. Ruthenium phthalocyanine (RuPc) was prepared by the procedure of Weber and Bush,[29] starting from ruthenium trichloride, phthalic acid and urea. Other metal complexes, organic substrates, chromatographic and spectroscopic standards were purchased from Aldrich. D_2O (D ≥ 99 %) was obtained from Isotec Inc.

Apparatus: Organic analyses by GC were performed on aliquots withdrawn with a microsyringe from the aqueous reaction mixtures and diluted 1:20 with diethyl ether, on a HP 6890 GLC instrument equipped with FID, using a 30-m HP-5 (0.32 mm i.d.; 0.25 μm film thickness) or a 30 m HP-Innowax (0.25 mm i.d.; 0.25 μm film thickness) capillary column with the injection port kept at 250 °C (carrier gas: He). The identity of each product was confirmed by comparison of the fragmentation pattern in the mass spectrum obtained with an MD 800 Fisons mass spectrometer operating in the electron ionization mode at 70 eV. ^{1}H NMR measurements were performed on a Bruker Avance 300 MHz spectrometer equipped with a BBO 5 mm probe, by adding small amount of D_2O to the reaction mixtures (1:3); water suppression was carried out by a presaturation sequence using a composite pulse (zgcppr Bruker sequence). A co-axial capillary tube containing a 30 mM solution of 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt (TSP) in water (D_2O) was used as reference. The identity of each product and their quantitation were confirmed by comparison of the position and intensity of suitable signals, by addition of measured amounts of pure compounds to the reaction mixtures.

Typical Procedure for the Hydration Reactions: The progress of the reactions was monitored by GC-MS and/or ^{1}H NMR spectroscopy; conversions, yields and rates were reproducible to within 10−15 %. We describe three different experimental procedures for the hydration reaction: (i) 2-propyn-1-ol, 3-butyn-2-ol, 1-phenyl-2-propyn-1-ol, 4-pentyn-1-ol, or 3-butyn-1-ol (equivalent to 400 mM of final solution) was added to an aqueous solution of RuPcS (10 mM) in a 5 mL vial in air or under a nitrogen atmosphere. The mixture was stirred for 24 h at 80 °C and analyzed by GC-MS and/or NMR spectroscopy. In the case of 1-phenyl-2-propyn-1-ol the reaction mixture was also treated with $CDCl_3$ (5 mL) and the extract analyzed by GC-MS and NMR spectroscopy; after the evaporation of the solvent, a polymeric film was obtained, which on the basis of IR analysis was shown to contain also polystyrene and/or styrene-based polymeric materials; (ii) the above substrates (400 mM) and RuHAP (78 mg/mL) in water were stirred at 80 °C for 24 h; the reaction mixtures were analyzed as above; (iii) 1,1-diphenyl-2-propyn-1-ol (400 mM) and RuPc (10 mM) in a water-saturated toluene solution were stirred at 80 °C for 24 h and directly analyzed by NMR spectroscopy and GC.

Hydration Reactions with D_2O: 2-Propyn-1-ol or 1-phenyl-2-propyn-1-ol (400 mM) and RuPcS (10 mM) or RuHAP (13.9 mg, 0.010 mmol) in D_2O (D ≥ 99.9 %) were reacted for 24 h at 80 °C. Hydroxyacetone, acrylic acid, 1-hydroxy-1-phenylacetone, cinnamaldehyde and styrene were detected by GC, GC-MS and NMR spectroscopy, either directly or, when necessary, after extraction with $CDCl_3$ from the reaction mixture; 3-hydroxypropanoic was directly analyzed only by NMR spectroscopy.

Detection of CO, Ethene and Propene: CO was captured by bubbling the evolved reaction gas through a CH_2Cl_2 solution of $[RuCl(dppp)_2]PF_6$; the amount of formed mono-carbonyl adduct $[RuCl(CO)(dppp)_2]PF_6$ was measured both by UV/Vis and IR analysis, by following the disappearance of the 460 nm band of the original complex or the appearance of the distinctive ν_{CO} absorption at 1930 cm^{-1} of the carbonyl adduct.[32] Although both UV and IR measurements might allow, in principle, the quantitation of the carbonyl adduct, and hence of the carbon monoxide produced, the quantitative results were erratic, probably due to the long reaction times required for the formation of the product. Ethene and propene were captured in a CH_2Cl_2 solution containing an excess of Br_2; the resulting 1,2-bromoalkane solutions were analyzed by GC, GC-MS and NMR spectroscopy, by comparing the results with those of the two commercial compounds (1,2-dibromoethane and 1,2-dibromopropane). Further qualitative data on the production of propene were obtained by headspace GC-MS analysis of the final reaction mixtures.

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