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Cyanohydrin Hydration with $[Ru(\eta^6-p-cymene)Cl_2PR_3]$ Complexes

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Supporting Information

ABSTRACT: The catalytic hydration of cyanohydrins to their corresponding α -hydroxyamides provides a route to industrially useful α -hydroxy amides, α -hydroxy esters, α -hydroxy carboxylic acids, and their acrylic derivatives. However, until now, no homogeneous nitrile hydration catalyst has been capable of complete conversion of cyanohydrins to their corresponding amides because cyanohydrins degrade to produce cyanide, which poisons the catalyst. Because the cyanohydrin degradation is an equilibrium process, it was hypothesized that a faster nitrile hydration catalyst would be



capable of hydrating the cyanohydrin before degradation occurs. Secondary coordination sphere effects were used to develop a faster catalyst based on the $[Ru(\eta^6\text{-arene})Cl_2(PR_3)]$ scaffold. A series of $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(PR_3)]$ complexes, where $R = NMe_2$, OMe, Et, was synthesized, and their activity toward cyanohydrin hydration was determined. The complex $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(P(NMe_2)_3)]$ is an excellent catalyst, and the unprecedented complete conversion of a cyanohydrin to its corresponding amide using a homogeneous catalyst was achieved with glycolonitrile and lactonitrile.

Methyl methacrylate and related derivatives of methacrylic acid are important monomers used in the production of acrylic plastics and in polymer dispersions for paints and coatings.^{1,2} The importance of these monomers to the world's economy is reflected in their production figures: global production of MMA in 2008 was an estimated 2.8 million metric tons and is projected to increase at an average annual rate of 3.3% during 2008-2013.3 The most widely used method for the production of methacrylates is the acetone cyanohydrin (ACH) process, shown in Scheme 1.4,5 The byproducts of this process include ammonium hydrogen sulfate (AHS) as well as acetone, acetone sulfonates, oligomers, and polymers. The AHS byproduct is a major problem for methacrylate producers. A typical ACH process generates about 2.5 kg of AHS per kg of methacrylate product. Consequently, disposing of the AHS (~7 million metric tons/year) or converting it requires considerable effort and expense. A common procedure is to pyrolyze the AHS at around 1000 °C, followed by other steps that eventually lead to sulfuric acid. This process is highly energy intensive and consumes large amounts of natural gas as fuel for the pyrolysis.⁶ In an alternative approach, the AHS is neutralized with ammonia to form ammonium sulfate, which has some limited use as a fertilizer. There is considerable expense and effort associated with both of these methods, and therefore the elimination of AHS would allow for considerable savings and improvement in the production of methacrylates. Consequently, there is a strong drive to find a replacement to the ACH process that does not involve sulfuric acid.

One route to a non sulfuric acid method involves the homogeneous catalytic hydration of acetone cyanohydrin.

Previously, we reported on a number of nitrile hydration catalysts, but in all cases these catalysts displayed only nominal hydration of acetone cyanohydrin and other cyanohydrins, including glycolonitrile, lactonitrile, mandelonitrile, cyclohexanone cyanohydrin, and 2-hydroxybutyronitrile.⁷ In every case, the poor activity of the catalyst toward cyanohydrins was caused by cyanide poisoning of the catalyst. (The cyanide comes from degradation of the cyanohydrin (Scheme 2).⁷) Because of cyanide poisoning, no catalyst has ever hydrated more than a minute quantity of acetone cyanohydrin in a homogeneous reaction.

Cyanohydrin degradation is a slow equilibrium process, and we reasoned that a faster catalyst would be less susceptible to poisoning. Previous research showed that for most nitrile hydration catalysts, the rate-limiting step in the catalytic cycle is the nucleophilic attack by water on the coordinated nitrile.⁸ To increase the rate of this step, we sought a way to simultaneously activate both the coordinated nitrile and the external water nucleophile. We hypothesized that a ligand with a better hydrogen-bond accepting group in the secondary coordination sphere should make a better nitrile hydration catalyst (Figure 1).

This hypothesis is based on the work of Grotjahn and coworkers, who showed that incorporation of hydrogen-bond accepting groups into the secondary coordination sphere of alkyne hydration catalysts can significantly enhance the rate of anti-Markovnikov alkyne hydration.^{9–11} To probe this hypothesis, we synthesized a series of [Ru(η^6 -p-cymene)-

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Scheme 1. ACH-Based Process for the Synthesis of Methacrylates



Scheme 2. Equilibrium between a Cyanohydrin and Its Corresponding Aldehyde/Ketone^a

$$\underset{O}{\overset{R}{\xrightarrow{}}} \overset{OH}{\xrightarrow{}} \overset{H_2}{\xrightarrow{}} \overset{M_2}{\xrightarrow{}} \overset{R}{\xrightarrow{}} \overset{OH}{\xrightarrow{}} \overset{O}{\xrightarrow{}} \overset{O}{\xrightarrow{}} \overset{H_2}{\xrightarrow{}} \overset{R}{\xrightarrow{}} \overset{OH}{\xrightarrow{}} \overset{R}{\xrightarrow{}} \overset{OH}{\xrightarrow{}} \overset{H_2}{\xrightarrow{}} \overset{R}{\xrightarrow{}} \overset{R}{\xrightarrow{}} \overset{H_2}{\xrightarrow{}} \overset{R}{\xrightarrow{}} \overset{$$

^{*a*}The cyanide coordinates to the metal catalyst (M) irreversibly.

Figure 1. Simultaneous activation of a coordinated nitrile and a noncoordinated hydrogen-bonding water molecule.

 $Cl_2(PR_3)$] complexes, (R = NMe₂ (1), OMe (2), Et (3)) and examined their ability to hydrate cyanohydrins.¹² The complex $[Ru(\eta^6-p\text{-cymene})Cl_2(P(NMe_2)_3)]$ was previously examined by Cadierno and co-workers, who found that the activity of the catalyst exceeded the activity of other ruthenium arene nitrile hydration complexes.¹³ A particular focus of our investigation was on determining if there was a correlation between the strength of the hydrogen bond accepting group in the secondary coordination sphere and the rate of nitrile hydration. The results of our study are reported herein.

Hydration of Acetonitrile. Initial nitrile hydration studies using 1-3 were conducted on acetonitrile at 100 °C and 5% catalyst loading. All three catalysts converted acetonitrile to acetamide, although 1 displayed considerably faster reactivity $(TOF = 35 h^{-1}(1), 0.41 h^{-1}(2), and 0.18 h^{-1}(3))$. As detailed in a footnote, the faster reactivity of 1 cannot be attributed to either steric or electronic effects,¹⁴ and the enhanced rate with 1 can likely be attributed to the hydrogen bond accepting ability of the tris(dimethylamino)phosphine ligand. To explore the role of H bonding in determining the relative rates of the hydration reactions, the ability of the catalysts to H bond to water was examined. To do this, the IR spectra of 1-3 were examined in wet KBr. The $\nu(OH)$ of water was observed at 3424, 3431, and 3441 cm⁻¹ for 1–3, respectively. Prior studies showed an excellent correlation between $\nu(OH)$ and the O–O bond distance in compounds containing O-H---O bonds; specifically, as the O–O bond distance decreased (indicating a stronger hydrogen bond), the $\nu(OH)$ frequency also decreased.¹⁵ On the basis of this analysis, the $\nu(OH)$ trend above indicates that the H bond strength to water follows the order 1 > 2 > 3. In addition to these solid-state studies, solution-phase IR studies were done with the complexes dissolved in THF using phenol as a H bond donor. The same general trend in $\nu(OH)$ was observed: i.e., $1 > 2 \cong 3$. (the solution-phase IR data are given in the Supporting Information). Thus, the hydration reactivity of the catalysts correlates with their ability to hydrogen bond to water: i.e., the best H bonding catalyst is the fastest catalyst. (Note that other methods have been developed to determine the relative strengths of hydrogen bond acceptors, including UV-vis

methods, NMR spectroscopy, and X-ray crystallography. These techniques and their application to these catalysts are discussed in more detail in the Supporting Information.)

Previous work showed that, in aqueous solutions, the cyanohydrin decomposition equilibrium favors cyanohydrins at low pH.^{16–18} Therefore, to limit cyanohydrin degradation (and subsequent cyanide poisoning), the cyanohydrin hydration reactions should be run at low pH. Because many nitrile hydration catalysts are only functional at high pH,⁸ the activity of 1 toward acetonitrile was investigated over a range of pH values (3.5–8.5). As the pH of the solution decreased, the rate of hydration decreased slightly from a TOF of 41 h⁻¹ at pH 8.5 to 25 h⁻¹ at pH 3.5,¹⁹ indicating that the catalyst should still be functional at pHs that are optimal for cyanohydrin hydration.

Hydration of Cyanohydrins. The cyanohydrin hydration reactions of glycolonitrile (4), lactonitrile (5), and acetone cyanohydrin (6) (Chart 1) were investigated under a variety of reaction conditions using catalysts 1-3.

Chart 1. Structures of Glycolonitrile (4), Lactonitrile (5), and Acetone Cyanohydrin (6)



As shown in Table 1, the only catalyst to hydrate glycolonitrile at any temperature was 1. For example, note in entry 3 that, at 25 °C and pH 8.5, glycolonitrile was completely hydrated within 43 h.²⁰ In comparison, the catalyst PtCl- $(PMe_2OH){PMe_2O_2H}$ only hydrated glycolonitrile to glycolamide with a 4% yield,⁷ making the hydration of glycolonitrile with 1 the first example of the complete conversion of a cyanohydrin to its corresponding amide using a homogeneous catalyst. To explore the effect of temperature, the hydration reactions were also carried out at 85 and 100 °C. At 85 °C (entry 2), the yield of glycolamide was 93% within 0.7 h; no further conversion was observed after that time. Increasing the temperature to 100 °C (entry 1) resulted in a lower net conversion (67%) but in only 0.2 h. No further reaction occurred after this time. In all cases, no formation of glycolic acid was observed. Needless to say, the decomposition of glycolonitrile to form equilibrium cyanide concentrations will be faster as the temperature is increased, and it is proposed that, at these higher temperatures, the complete cessation of activity is due to cyanide poisoning.

Reactions using either catalyst 2 or 3 did not show any conversion of glycolonitrile to glycolamide at any temperature.

Table 1. Glycolonitrile Hydration Results Using $[Ru(\eta^6-p-cymene)Cl_2(P(NMe_2)_3)]$, $[Ru(\eta^6-p-cymene)Cl_2(P(OMe)_3)]$, and $[Ru(\eta^6-p-cymene)Cl_2(PEt_3)]^a$

entry	cat.	reacn temp (°C)	hydration (%) ^b	reacn time (h)
1	$\begin{bmatrix} \operatorname{Ru}(\eta^6\text{-}p\text{-}\operatorname{cymene}) \\ \operatorname{Cl}_2(\operatorname{P}(\operatorname{NMe}_2)_3) \end{bmatrix}$	100	67	0.2
2	$\begin{bmatrix} \operatorname{Ru}(\eta^6\text{-}p\text{-}cymene) \\ \operatorname{Cl}_2(\operatorname{P}(\operatorname{NMe}_2)_3) \end{bmatrix}$	85	93	0.7
3	$\begin{bmatrix} \operatorname{Ru}(\eta^6\text{-}p\text{-}\operatorname{cymene}) \\ \operatorname{Cl}_2(\operatorname{P}(\operatorname{NMe}_2)_3) \end{bmatrix}$	25	>99	43
4	$\begin{bmatrix} \operatorname{Ru}(\eta^6\text{-}p\text{-}cymene) \\ \operatorname{Cl}_2(\operatorname{P}(\operatorname{OMe})_3) \end{bmatrix}$	85	0	1
5	$\begin{bmatrix} \operatorname{Ru}(\eta^6\text{-}p\text{-}\operatorname{cymene}) \\ \operatorname{Cl}_2(\operatorname{P}(\operatorname{OMe})_3) \end{bmatrix}$	25	0	43
6	$\begin{bmatrix} \operatorname{Ru}(\eta^6\text{-}p\text{-}\operatorname{cymene}) \\ \operatorname{Cl}_2(\operatorname{PEt}_3) \end{bmatrix}$	85	0	1
7	$\begin{bmatrix} \operatorname{Ru}(\eta^6\text{-}p\text{-}\operatorname{cymene}) \\ \operatorname{Cl}_2(\operatorname{PEt}_3) \end{bmatrix}$	25	0	43
8	$\frac{PtCl(PMe_2OH)}{\{(PMe_2O)_2H\}^c}$	25	4	52.6

^{*a*}Reactions performed under an N₂ atmosphere in D₂O with 0.15 M glycolonitrile, pH 8.5, and 7.5 mM catalyst (5% catalyst loading). ^{*b*}Yields determined by ¹H NMR. No formation of glycolic acid was observed for any glycolonitrile hydration trial. No evidence of H–D exchange of the α -nitrile protons was observed. ^{*c*}See ref 7.

Because these catalysts are slower, it is proposed that catalyst poisoning occurs before hydration.

The hydration reactions of lactonitrile and acetone cyanohydrin, cyanohydrins both sterically bulkier than glycolonitrile, with catalyst 1 were investigated (Table 2). At 25 °C, pH 3.5, and 5% catalyst loading, lactonitrile was completely converted to lactamide in approximately 110 h. Consistent with the prior observation that cyanohydrin decomposition increases at higher pH, at pH 8.5 the yield was only 13% in 61 h with no further conversion after that time (Table 2, entry 4).

In the case of acetone cyanohydrin, many different conditions were employed in an attempt to effect complete hydration (Table 2). However, no conditions were found that resulted in complete conversion. For example, at pH 3.5, a 9% conversion to α -hydroxyisobutyramide was obtained after 5 days. This conversion increased slightly as the pH was lowered:

at pH 3.0, the yields were 14% (25 °C) and 15% (70 °C) in a 10.6 M acetone solution. Although not a complete conversion, this is the best yield that has been observed for the hydration of acetone cyanohydrin with any homogeneous nitrile hydration catalyst. As expected, these conversions decreased as the pH increased. Thus, at pH 8.5 and 25 °C, no conversion of acetone cyanohydrin to α -hydroxyisobutyramide was observed, even after several weeks. The absence of reactivity is attributed to cyanide poisoning of the catalyst. To drive the equilbrium back, acetone was added to the reaction mixture at pH 8.5, but still no hydration was observed.

Catalyst Degradation. Previous investigations done by Cadierno and co-workers showed that, under aqueous conditions, the $[Ru(\eta^6-arene)Cl_2(P(NMe_2)_3)]$ complexes completely degraded within 48 h at room temperature to form $[Ru(\eta^6-arene)Cl_2(HNMe_2)]$, as evidenced by the formation of several peaks in the ³¹P NMR spectra, as well as the formation of a broad singlet around 2.6 ppm in the ¹H NMR spectra.¹³ Additionally, when $[Ru(\eta^6-p-cymene) Cl_2(HNMe_2)$] and $[Ru(\eta^6-p-cymene)Cl_2(P(NMe_2)_3)]$ were used to hydrate benzonitrile at 100 °C and 5% catalyst loading, the activity of $[Ru(\eta^6-p-cymene)Cl_2(HNMe_2)]$ was much lower than $[Ru(\eta^6-p-cymene)Cl_2(P(NMe_2)_3)]$, with TOFs of <1 and 4 h^{-1} , respectively.¹³ The stability of 1 was also investigated during cyanohydrin hydration, not only because the catalyst was previously shown to degrade but also because cyanide can react with the catalyst to poison it. Over the course of hydration of acetonitrile, glycolonitrile, lactonitrile, and acetone cyanohydrin, several unidentified peaks were observed in the ³¹P NMR spectrum. These spectra are given in the Supporting Information. Arene loss was only observed when catalyst activity ceased during the hydration of cyanohydrins. No arene loss was observed in the hydration of acetonitrile.²

Conclusions. Catalytic cyanohydrin hydration is challenging, because cyanohydrins degrade to produce HCN (and cyanide), which poisons homogeneous nitrile hydration catalysts. Because cyanohydrins are always going to be in equilibrium, faster nitrile hydration catalysts need to be developed. Following the hypothesis that a catalyst that contains ligands with hydrogen bond accepting groups will be faster, the nitrile hydration catalyst [Ru(η^6 -p-cymene)Cl₂(P-(NMe₂)₃)] was investigated. This catalyst was an excellent

entry	cyanohydrin	$cosolvent^b$	[cosolvent] (M)	[cyanohydrin] (M)	[catalyst] (mM)	pН	reacn temp (°C)	calcd [HCN] @ equilibrium (mM) ^c	$\stackrel{\rm hydration}{(\%)^d}$	reacn time (h)
1	glycolonitrile			0.15	7.6	8.5	100	0.07	67	0.2
2	glycolontrile			0.15	7.6	8.5	25	0.07	>99	49
3	lactonitrile			0.16	7.8	8.5	100	26.3	10	0.2
4	lactonitrile			0.15	7.6	8.5	25	25.4	13	61
5	lactonitrile			0.15	7.6	3.5	25	2.01	>99	112
6	lactonitrile	acetaldehyde	0.3	0.15	7.5	3.5	25	0.00	>99	109
7	ACH			0.16	8.8	8.5	25	160	0	478
8	ACH	acetone	12.1	0.15	8.7	8.5	25	127	0	478
9	ACH	acetone	11.2	0.15	7.5	3.5	25	0.95	9	118
10	ACH	acetone	10.6	0.15	7.5	3.0	95	1.01	6	22
11	ACH	acetone	10.6	0.15	7.5	3.0	70	1.01	15	22
12	ACH	acetone	10.6	0.15	7.5	3.0	25	1.01	14	149

Table 2. Selected Cyanohydrin Hydration Results Using $[Ru(\eta^6-p-cymene)Cl_2(P(NMe_2)_3)]^a$

^{*a*}Reactions performed under an N₂ atmosphere in water (H₂O or D₂O) with 5% catalyst loading. ^{*b*}Cosolvent is any solvent not including water. No deuterated cosolvents were used. ^{*c*}Concentration of cyanide at equilibrium was calculated using published equilibrium constants.¹⁶ ^{*d*}Yields determined by ¹H NMR. No formation of carboxylic acid byproduct was observed in any cyanohydrin hydration trial. No evidence of H–D exchange of the α -nitrile protons was observed.

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nitrile hydration catalyst and completely hydrated glycolonitrile and lactonitrile. This catalyst also hydrated acetone cyanohydrin (15% conversion to the amide product). These are the highest conversions of cyanohydrin to amide product with a homogeneous catalyst and, in the case of glycolonitrile and lactonitrile, are the first examples of complete conversion of cyanohydrins to their corresponding amides using a homogeneous nitrile hydration catalyst. Further mechanistic work, including investigation of other complexes containing hydrogen bond accepting groups and DFT calculations of the hydrogen bonding interactions, is currently underway.

ASSOCIATED CONTENT

S Supporting Information

Text, a table, and figures giving experimental procedures, a discussion of techniques for determining H bond acceptor strength, solution-phase IR data, and 31 P NMR spectra and data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(20) A control reaction showed that the rate of acetonitrile hydration with 3 is 2 orders of magnitude faster at pH 8.5 than at pH 5.0, presumably because of the higher concentration of hydroxide, which is more nucleophilic than water. Additionally, the equilibrium constants for glycolonitrile degradation are $K_{\rm pH9.0} = 3.29 \times 10^{-8}$ and $K_{\rm pH4.0} = 1.09 \times 10^{-9}$. Because there is little difference in the position of the glycolonitrile equilibrium at high pH, all glycolonitrile hydration trials were conducted at pH 8.5.

(21) Cadierno and co-workers found that addition of 200 equiv of free arene ligand led to a decrease in the rate of benzonitrile hydration with $[Ru(\eta^{6}\text{-arene})Cl_{2}(P(NMe_{2})_{3})]$ when arene = $C_{6}H_{6}$, toluene, *p*-cymene, mesitylene. However, in these cases, the arene could potentially competitively coordinate to the catalyst by η^{2} -arene coordination, decreasing the rate of nitrile hydration.