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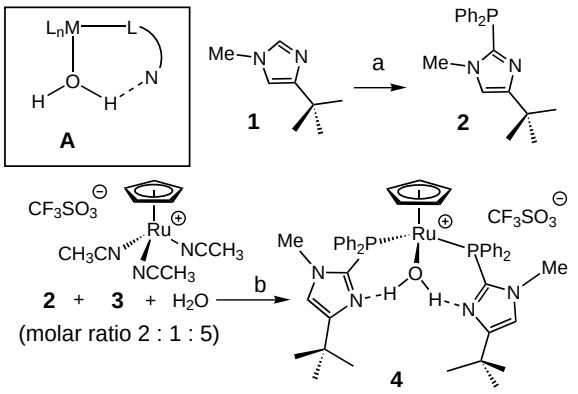
[15] IR spectra of V_2O_5/C-PEG products showed three strong vibrations at 1000, 760, and 521 cm^{-1}, identical to those of V_2O_5 xerogel. In the CH_2 stretching absorption region, the strong band at 2877 cm^{-1} observed in bulk PEG is split into two bands at 2924 and 2854 cm^{-1}. In the region 1500–1000 cm^{-1}, no significant energy shifts were observed with respect to bulk PEG, but the relative intensities of the absorption bands were different and the band shapes were broader. The XRD and IR results confirmed that PEG was inserted into the V_2O_5 layers, and the insertion did not affect the structural integrity of the V_2O_5 framework.

[16] Chemical composition for x(Li) for all materials were calculated from the formula weight of the materials determined by thermogravimetric and chemical analyses [%]; for V_2O_5/C-PEG: V_2O_5: 72.5, C: 12.1, PEG: 6.03; for V_2O_5/C: V_2O_5: 72.1, C: 16.6.

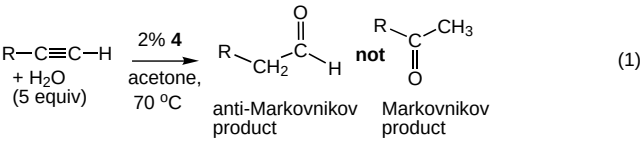
Combined Effects of Metal and Ligand Capable of Accepting a Proton or Hydrogen Bond Catalyze Anti-Markovnikov Hydration of Terminal Alkynes**

Douglas B. Grotjahn,* Christopher D. Incarvito, and Arnold L. Rheingold

Metalloenzyme catalysts such as carboxypeptidase use the cooperative effects of a metal ion and suitably placed organic functional groups capable of proton transfer or hydrogen bonding.[1, 2] Using this cue from Nature, we are making complexes of general structure **A** (Scheme 1) where L is a ligating atom and N is part of a heterocycle, particularly imidazole. Our results clearly indicate that the combined effects of a metal and a proton or hydrogen bond acceptor as in **A** produce a binding pocket for a polar ligand. We report herein on the anti-Markovnikov hydration of terminal alkynes [Eq. (1)], which produces aldehydes, rather than the isomeric ketones, with selectivities of up to 1000 to 1.



Scheme 1. Design (**A**) and synthesis of catalyst **4**. a) *n*BuLi, THF, −78 to −50 °C, 3 h, then $ClPPh_2$, warming to RT, 51 %; b) $CDCl_3$ or CH_2Cl_2, RT, <2 h, 98 %.



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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

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Traditional methods of hydrating alkynes require catalysis by strong acids and environmentally objectionable Hg^{II}, or transition metal salts. All of these conditions give Markovnikov addition of water to the terminal alkyne, leading to the formation of the methyl ketone.[3–9] Anti-Markovnikov hydration can be achieved indirectly by stoichiometric hydroboration or hydrosilation, followed by oxidation.[10] Bruneau and Dixneuf recently reviewed anti-Markovnikov addition of weak nucleophiles with N–H or O–H bonds to terminal alkynes.[11] Thus far, however, there have been only two reports of catalytic anti-Markovnikov *hydration* of terminal alkynes. In 1998, Tokunaga and Wakatsuki[12] found after trying about 20 phosphanes that the combined use of $[(C_6H_6)RuCl_2(C_6F_5PPh_2)]$ (10 mol%) and $C_6F_5PPh_2$ (30 mol%) gave aldehydes in 50–75% yield, with typical aldehyde-to-ketone selectivities of about 10 to 1. Hindered alkynes such as phenyl- or *tert*-butylacetylene gave less than 2% yields of product. This year the same group reported improved results with chelating or electron-rich, small phosphanes on the CpRuCl fragment.[13] For example, in favorable cases 1–2 mol% of $[CpRuCl(Me_2PCH_2PMe_2)]$ or $[CpRuCl(PMe_3)_2]$ could be used in 2-propanol/water at 100 °C. In some cases 10 mol% of catalyst was needed, moreover nitriles inhibit the reaction.

In contrast, here we report that electron-rich phosphanes are not needed. Significantly, hydrogen bonding in catalyst **4** (Scheme 1) leads to hydration of even *tert*-butylacetylene at the 2 mol% level, giving yields in excess of 90%. Advantages of **4** over the other Ru^{II} catalysts reported include a lack of inhibition by nitriles, and the tolerance of acid-sensitive propargylic ether substituents.

Pursuing the design outlined above, we made the phosphinoimidazole ligand **2** (Scheme 1) by deprotonation of **1**[14, 15] at C-2, followed by quenching with $ClPPh_2$.[16] We found that two moles of **2** rapidly react with **3**[17] in the presence of five equivalents of water to give (after crystallization) a 98% yield of catalyst **4**. The presence of a ^1H NMR signal near $\delta = 9.1$ (slightly broad singlet, 2H, H_2O–Ru) and satisfactory elemental analysis suggested that a water molecule was indeed coordinated to the metal center. However, unequivocal verification of the water molecule in the catalyst binding pocket was provided by an X-ray crystal structure determination (Figure 1).[18] A piano-stool structure supports the *cis* coordination of the two phosphane ligands (P-Ru-P angle 97.77(3)°), the third leg of the stool consisting of the Ru–O bond (P-Ru-O angles 91.89(3) and 93.30(9)°). Of special interest for catalyst design, both (located) hydrogen atoms of the bound water molecule engage in hydrogen bonding to the two imidazoles, with N···H distances of 1.638(6) and 1.802(8) Å.

Gratifyingly, only 2 mol% of complex **4** catalyzed the clean conversion of 1-hexyne (Table 1, entry 1) to hexanal at temperatures near 70 °C. Reaction progress was monitored by ^1H NMR spectroscopy by using an internal standard. Within 1.5 days, consumption of alkyne was complete, and hexanal had been formed in 96% yield. NMR spectroscopy showed that about half the catalyst remained intact. No peaks for the Markovnikov product 2-hexanone were evident in the 500 MHz ^1H NMR spectra, but to verify this result, 1% of an authentic sample was added. A very small peak increased in size, such that we estimate that only 0.1% of 2-hexanone had been present before addition of authentic material, meaning that the aldehyde-to-ketone ratio was 1000 to 1. Our results compare favorably with those of Tokunaga and Wakatsuki with the same alkyne.[12, 13] Moreover, Table 1 shows that **4** works with a wide variety of substrates, giving high selectivities. Alkyl-substituted alkynes work the best (Table 1, entries 1–3, 6–8). A *tert*-butyl group (Table 1, entry 3) slows hydration but on heating at 88–91 °C,

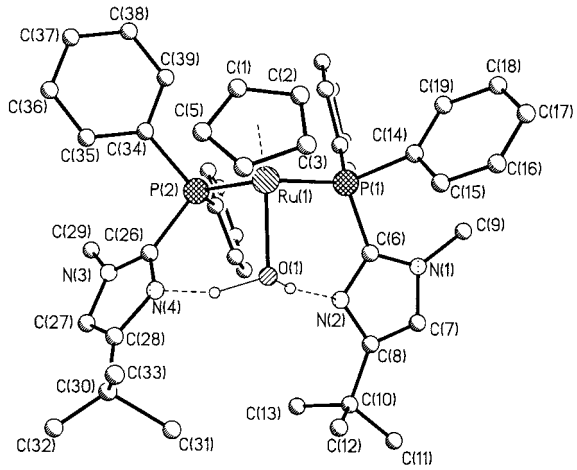


Figure 1. X-ray crystal structure of the cation of **4** (thermal ellipsoids are at 30% probability). The $CF_3SO_3^-$ counterion is not shown for clarity. Key bond lengths [Å] and angles [°]: Ru(1)-O(1) 2.164(3), Ru(1)-P(1) 2.3043(10), Ru(1)-P(2) 2.3251(10), Ru(1)-Cp(centroid) 1.836(4), N(2)-H 1.802(8), N(4)-H 1.638(6); P(1)-Ru(1)-P(2) 97.77(3), P(1)-Ru(1)-O(1) 93.30(9), P(2)-Ru(1)-O(1) 91.89(8).

Table 1. Catalysis of alkyne hydration [see Eq. (1)].[a]

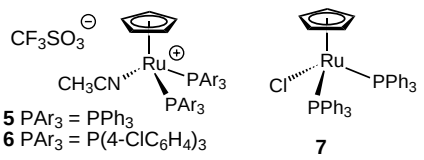
Entry	Catalyst	Alkyne substituent R	Aldehyde yield [%] after reaction time 3 h	21 h	later [h]	Selectivity[b]
1	**4**	Bu	39	92	96 [36]	1000
2	**4**	$PhCH_2CH_2$	40	88	92 [46]	150
3	**4**	$(CH_3)_3C$	3.5	21	91[c]	≥130
4	**4**	Ph	9.6	20	54[d]	135
5	**4**	Ph[e]	24	64	75 [42]	32
6	**4**	TBSO-CH_2[f]	28	91	96 [36]	≥200
7	**4**	THPO-CH_2[g]	35	83	86 [50]	≥400
8	**4**	$NC(CH_2)_3$	34	96	98 [40]	n.d.[h]
9	**5**	Bu	0.1	0.3	n.d.	n.d.
10	**6**	Bu	0.3	0.5	n.d.	n.d.
11	**6** + **1**	Bu	<0.1	<0.1	n.d.	n.d.
12	**6** + Et_3N	Bu	0	0	n.d.	n.d.
13	**7**	Bu	0.3	1.0	1.2[i]	n.d.

[a] Conditions: 0.5 mmol alkyne, 5 equiv water, 2 mol% catalyst, and $(Me_3Si)_4C$ internal standard in $[D_6]$acetone (1 mL) heated in a sealed NMR tube in an oil bath (67–72 °C). Yields and products identified by ^1H and in some cases ^{13}C NMR data. See Supporting Information for full details. [b] Ratio of aldehyde (value shown) to ketone (assigned value of 1). Authentic sample of ketone added at end of reaction period. See Supporting Information for full details. [c] Yield 49% after 68 h; 91% after an additional 108 h at 88–91 °C. [d] Yield 54% after three additions of 2 mol% **4** and 36–45 h heating each time. [e] Using 10 mol% catalyst with substrate concentration of 0.2 M. [f] TBS = $(CH_3)_2(t\text{Bu})Si$. [g] THP = 3,4,5,6-tetrahydropyran-2-yl. [h] n.d. = not determined. [i] After 7 d at 90 °C.

trimethylacetaldehyde is formed in 91% yield. Phenylacetylene reacts about as sluggishly as *tert*-butylacetylene, but in this case NMR spectroscopy confirms that 2 mol% **4** (Table 1, entry 4) disappears after 21 h and hydration stops at about 30% conversion unless additional catalyst is added, eventually producing 54% aldehyde. Alternatively (Table 1, entry 5), starting with 10 mol% **4**, improved yield and rate are obtained.

A nitrile does not affect the catalyst (compare entries 8 and 1 in Table 1). Even alkynes with acid-sensitive alcohol protecting groups (Table 1, entries 6 and 7) are hydrated to give aldehydes made previously in multistep syntheses.[19] Remarkably, neither an allenylidene complex nor propargyl alcohol (a potential hydrolysis product) are formed.[20]

Several control experiments show that the imidazole groups play a key role in the catalysis. First, in hydration of 1-hexyne, simple triarylphosphane ligands of slightly different electronic properties on the $[CpRu]^+$ ion (**5** and **6**; Table 1, entries 9 and

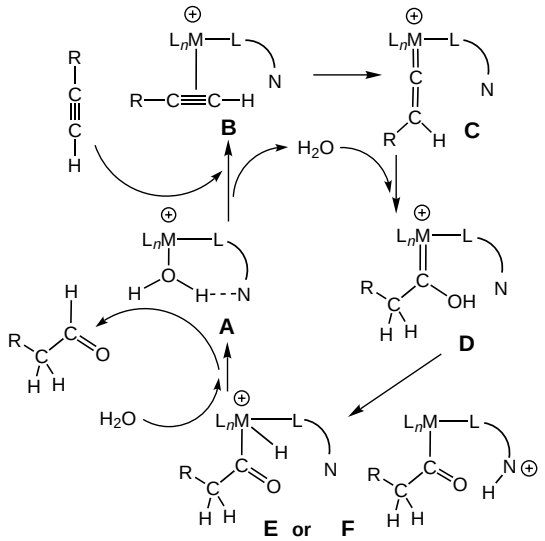


5 $PAr_3 = PPh_3$
6 $PAr_3 = P(4\text{-}ClC_6H_4)_3$

7

10, respectively) give less than 0.5% yields of hexanal, with no 2-hexanone being detected.[21] Further, if the imidazole groups function merely as a base, their placement in **4** is crucial: addition of 2 mol (per Ru center) of either the hindered imidazole base **1** or Et_3N to mixtures containing **6** led to virtually no production of aldehyde (Table 1, entries 11 and 12). Finally, complex **7** is also ineffective (Table 1, entry 13).

As to the probable mechanism of the alkyne hydration, ketones may come from attack of water on C-2 of alkyne π complexes (**B**, Scheme 2).[22] In contrast, for aldehyde formation, likely intermediates include complexes with ligands



Scheme 2. Probable intermediates and mechanism of alkyne hydration.

such as alkyne, vinylidene (**C**), hydroxycarbene (**D**), or related, tautomeric acyl and hydride (**E**).[23] Any of the conversions between these species conceivably could be aided by the presence of the imidazole groups or their protonated forms (e.g., **F**).[24] Alternatively, the hydrogen bonding in **4** may stabilize the catalyst. Judging from the lack of catalytic reactivity of other $\{CpRu(PAr_3)_2\}$ fragments under the conditions used (e.g., Table 1 entries 9–13 and ref. [23b]), the effects of R = imidazol-2-yl are especially intriguing and are the subject of ongoing studies. We note that the most recent CpRuCl-based catalyst was inhibited by a nitrile-containing alkyne;[13] the lack of inhibition of **4** may be related to the ability of **4** to exclude a coordinated nitrile in its resting state (**A**, Scheme 2).

In conclusion, regardless of mechanism, we provide clear evidence that the combined effects of a Ru^{II} center and imidazolylphosphanes create an excellent single-component catalyst for the anti-Markovnikov hydration of terminal alkynes under near-neutral reaction conditions. We are currently extending our design principle to other structures and reactions.

Experimental Section

Preparation of catalyst **4**: Deoxygenated solvents were used in an M. Braun glovebox. To solid phosphane **2** (120.0 mg, 0.372 mmol) and $[CpRu(CH_3CN)_3OSO_2CF_3]$ (**3**; 78.3 mg, 0.179 mmol) was added CH_2Cl_2 (3 mL). Water (16 μL, 0.89 mmol) was added and the resulting solution was stirred for 2 h before being concentrated in vacuo. The residual orange gum was dissolved in acetone (2 mL) containing water (16 μL) and the resulting solution transferred to a tared vial. The vial was placed in a small jar containing hexanes. After one day, crystals of **4** had formed and the supernatant was removed from them by pipet. The crystals were rinsed with hexanes and placed under vacuum, leaving orange crystals and powder (172.2 mg, 98% yield). ^1H NMR ([D$_6$]acetone, 500 MHz): $\delta = 9.12$ (sl br s, 2H), 7.54–7.58 (m, 4H), 7.49–7.54 (m, 2H), 7.32–7.41 (m, 6H), 7.17 (s, 2H), 7.13 (sl br t, $J = 7.5$ Hz, 4H), 7.01 (sl br dd, $J = 8.5$, 10 Hz, 4H), 4.19 (s, 5H), 2.85 (s, 6H), 1.36 (s, 18H); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 80.95 MHz): $\delta = 26.72$ (br s); elemental analysis (%) calcd for $C_{46}H_{53}F_3N_4O_4P_2RuS$ (978.03): C 56.49, H 5.46, N 5.73; found: C 56.39, H 5.21, N 5.79.

Example of procedure used to monitor alkyne hydration: Conversion of 4-phenyl-1-butyne to 4-phenylbutanal (Table 1, entry 2): In the glovebox, catalyst **4** (9.8 mg, 0.010 mmol) and internal standard $(Me_3Si)_4C$ (0.5 mg) were added to a vial. Using portions of [D$_6$]acetone (total volume 0.7 mL), the solid complex and standard were transferred by pipet to a resealable NMR tube. Not all **4** had dissolved at this point, so the transfer using solvent was partially mechanical. Water (45 μL, 2.5 mmol) was added, followed by $PhCH_2CH_2CCH$ (64.6 mg, 0.496 mmol) and enough [D$_6$]acetone to bring the total volume to 1.0 mL. The tube was sealed, removed from the glovebox, and briefly placed in a sonicating bath to dissolve all the catalyst to form a pale orange-yellow solution. The ^1H NMR spectrum of the resulting solution was recorded at this point and at intervals during heating of the NMR tube, using the same conditions (Varian 500 MHz spectrometer, four 30° pulses, 120 s delays between pulses). Monitoring reactions by NMR spectroscopy rather than by GC allowed us to determine if catalyst was still present. After 46 h, a sample of 4-phenyl-2-butanone (2 μL, 0.013 mmol, 0.027 times the amount of alkyne added) was added to the NMR tube. A small singlet (ascribed to the methyl protons of the ketone) at $\delta = 2.086$ grew in size. The increase in the singlet's integral indicated an aldehyde-to-ketone ratio of 150 to 1 before ketone addition. For the less volatile aldehydes made in entries 6 and 7 in Table 1, the mixture was worked up to provide pure aldehyde. Full details of these experiments are available in the Supporting Information.

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Metal-Catalyzed Selective Deoxygenation of Diols to Alcohols**

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Design and discovery of new catalysts that operate by nontraditional mechanisms offer the possibility of efficient and selective transformations that are difficult to achieve by conventional methods. Reactions proceeding through ionic mechanisms are attractive targets for development in this context. The traditional homogeneous catalytic hydrogenation of carbonyl groups[1] involves the coordination of a ketone or aldehyde substrate to a metal center and insertion of the C=O bond into a metal hydride bond. In ionic hydrogenations, hydrogen gas is heterolytically cleaved by a metal complex and then added to an unsaturated organic compound through proton (H^+) and hydride (H^-) transfer steps. We recently reported Mo and W catalysts for ketone hydrogenation that operate by an ionic hydrogenation pathway under mild conditions.[2] Magee and Norton discovered a Ru system that catalyzes the enantioface-selective hydrogenation of C=N bonds by an ionic mechanism.[3] Shvo and co-workers reported a remarkable series of reactions catalyzed by ruthenium complexes with phenyl-substituted cyclopentadienone ligands,[4] and recent studies by Casey et al. demonstrated that the proton and hydride transfer are concerted in such systems.[5] The remarkably reactive Ru hydrogenation catalysts of Noyori and co-workers are now thought to proceed by a related mechanism in which H_2 is cleaved to form M–H and N–H bonds.[6]

Synthetic procedures for deoxygenation of alcohols[7] generally involve multiple steps and low atom efficiencies.[8] *Selective* deoxygenation of one of the two OH groups of diols presents an even more formidable challenge than the deoxygenation of alcohols. Vicinal OH functionalities represent a ubiquitous feature of compounds derived from carbohydrates, but diols and polyols are unsuitable precursors for many industrial applications because they are overfunctionalized with an abundance of OH groups of very similar reactivity. Conversion of biomass to useful industrial chemicals[9] offers an attractive solution to consumption of petroleum-based resources, an aspect of growing concern. We

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