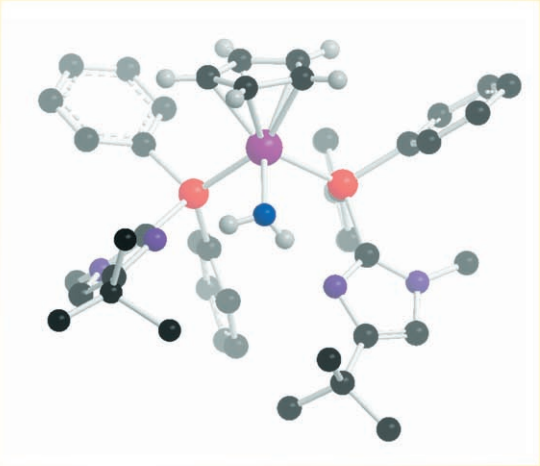
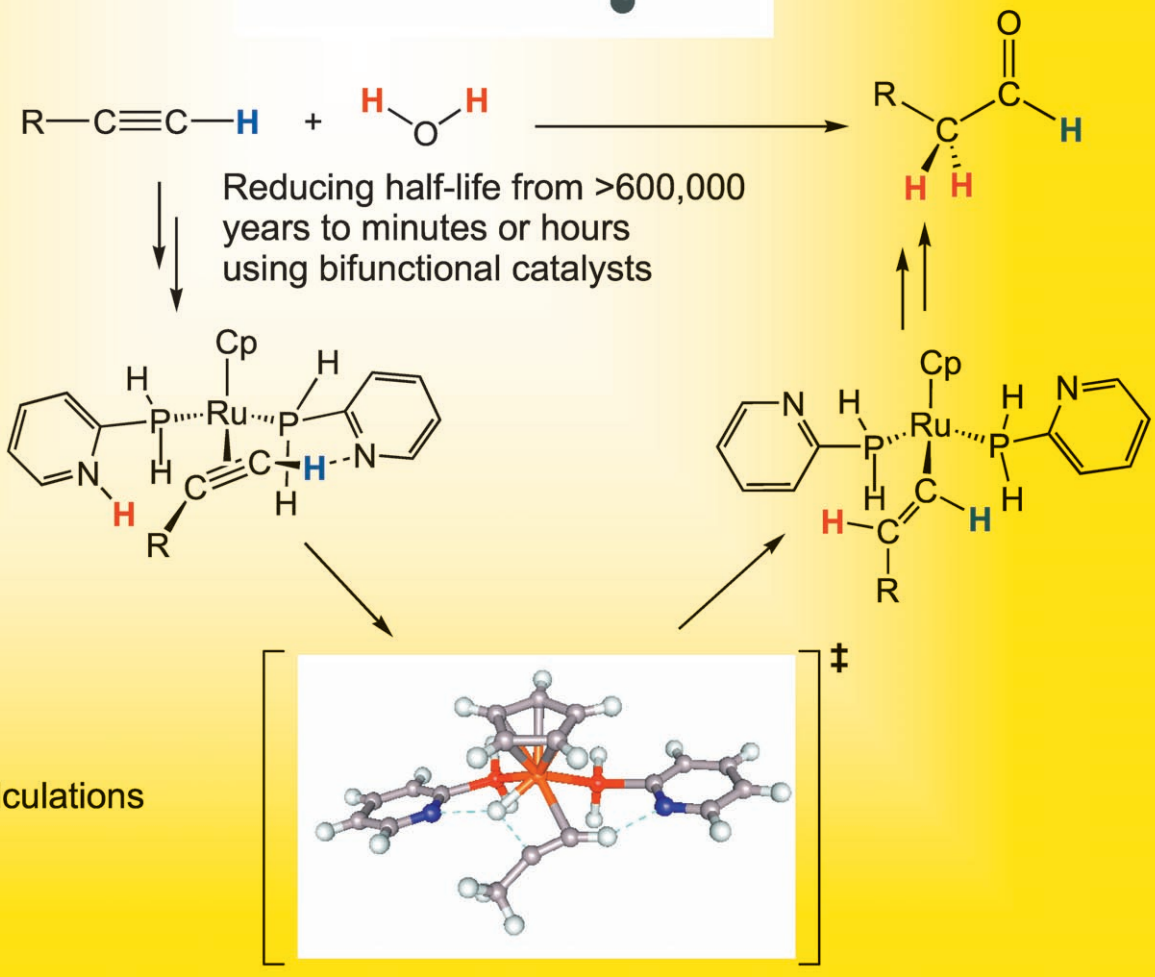
Bifunctional Organometallic Catalysts Involving Proton Transfer or Hydrogen Bonding

From experiment...





...to calculations

DOI: 10.1002/chem.200500253

Bifunctional Organometallic Catalysts Involving Proton Transfer or Hydrogen Bonding

Douglas B. Grotjahn*[a]

Abstract: Inspired by the cooperativity displayed by metalloenzymes, bifunctional organometallic complexes featuring pendant basic functional groups are designed and evaluated as catalysts in reactions for which enzymes are not suited. Anti-Markovnikov hydration of terminal alkynes is the focus, as are hydrogen bonding and proton transfer facilitated by the pendant groups.

Keywords: cooperative effects · homogeneous catalysis · hydrogen bonds · P ligands · proton transfer

Introduction

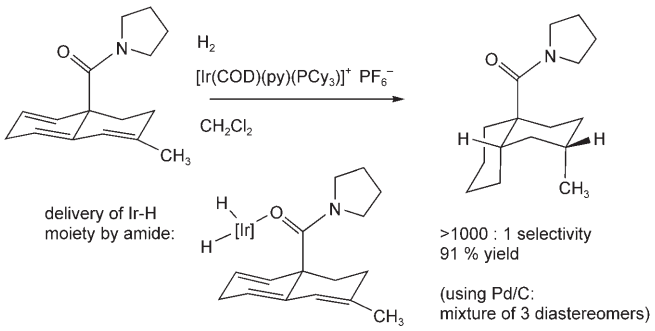
In 1823 Döbereiner ignited more than curiosity, when he discovered the ability of platinum black to cause a stream of hydrogen gas to catch fire.[1] Berzelius considered this experiment when he coined the term catalysis in 1835. Catalysis is a field that inspires wonder: reactions impossible in the absence of catalyst are made possible as if by magic. Catalysis is now also of tremendous practical importance and financial value, by one account[2] at the core of 90% of current chemical processes and producing more than half of today's chemical products. The development of new catalysts for making important organic compounds, especially those operating by new mechanisms, has not only intellectual appeal and excitement, but also far-reaching practical and political importance.

The fascination with elemental metals and hydrogen continued with the discovery of heterogeneous hydrogenation catalysts in the latter part of the 19th century.[1] In the middle of the 20th century, early structure and bonding studies of organometallic complexes were followed in the 1960s[3–5] by the development of practical homogeneous hydrogenation catalysis by Wilkinson[6] and the discovery of enantioselective catalysis by Noyori[5] and Knowles.[7]

In the ensuing 40 years, most efforts to improve organometallic catalysts have focused on variations in the metal used and the steric and electronic properties of the ligands attached. These three factors have tremendous influence on the affinity of the potential catalyst for reactants, intermediates, and products and on the rates of reactant conversion to products. For example, the original Rh and Ir hydrogenation catalysts discovered by Wilkinson and Osborn featured two or three triphenylphosphine ligands, of which generally two stay on the metal. However, by changing to one large and strongly-binding phosphine, Crabtree and co-workers created a catalyst with high affinity for existing polar groups in the hydrogenation substrate, allowing precise directing of the catalyst by temporary coordination to the substrate (Scheme 1).[8,9]

From Enzymes to Organometallics

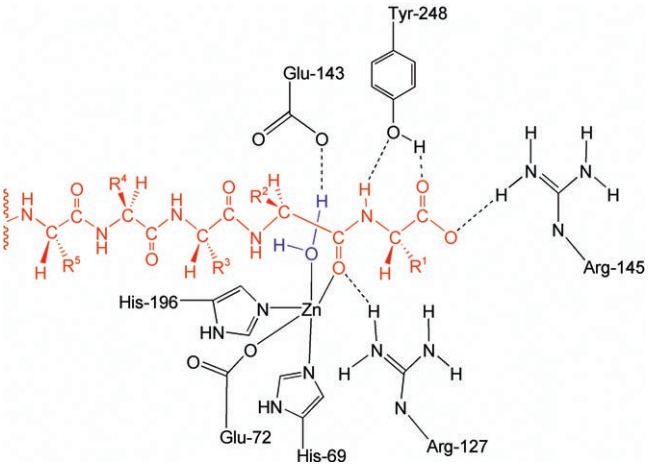
In general, organometallic studies have focused on a single metal, or small cluster of metals, and its steric and electronic



Scheme 1. Precise delivery of hydrogen by catalyst.

[a] Prof. D. B. Grotjahn
Department of Chemistry and Biochemistry
San Diego State University
5500 Campanile Drive
San Diego, CA 92182–1030 (USA)
Fax (+1) 619-594-4634
E-mail: grotjahn@chemistry.sdsu.edu

environment. In contrast, natural enzymatic catalysts often use a number of interactions to achieve efficiency and selectivity. One class of metalloenzymes features a single metal center along with various acidic and basic organic functional groups.[10] Scheme 2 illustrates this class, with interactions

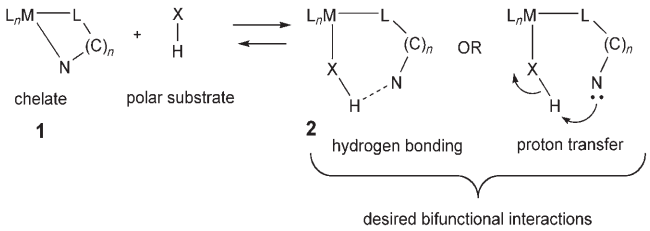


Scheme 2. Proposed cooperativity in the active site of carboxypeptidase. Hydrogen bonds are indicated by dashed lines.

proposed for the active site of the amide hydrolysis catalyst carboxypeptidase. The Zn^{II} center is coordinated to the enzyme active site through two histidine imidazole groups and one carboxylate group, leaving it to act as a Lewis acid toward the amide carbonyl to be hydrolyzed and the water molecule that performs the hydrolysis. Other hydrogen-bonding interactions are thought to help the carboxy terminus of the substrate to bind to the active site, and proton transfer from bound water to the carboxylate of Glu-143 is thought to facilitate an attack of water on the amide bond. Fortunately for protein-based life, in the absence of catalyst, amide-bond hydrolysis at ambient temperatures has a half-life of 350 to 500 years.[11,12] Remarkably, carboxypeptidase completes the task in seconds, achieving an acceleration of more than 10^{11}. What can we learn from this? Can we apply some of the design principles of nature to organometallic catalysis, for reactions to which enzymes are not suited?

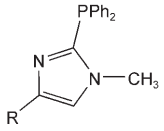
Attempts to improve organometallic catalysis by using a variety of secondary interactions have been increasingly studied in the past 25 years.[13–16] In enzymatic catalysis, hydrogen bonding and proton transfer are common themes. Hydrogen bonding helps determine the structure and function of nature's polymers (DNA, RNA, and proteins). In the serine proteases, a proposed role of the basic imidazole of a histidine side-chain is to deprotonate water during amide hydrolysis.[10] Fascinating studies, especially in the past 10 years,[17–19] have focused mostly on structural aspects of organometallic hydrogen bonding, revealing new hydrogen-bonding interactions, such as M–H···H–D and M···H–D (D = hydrogen bond donor). As for catalysis, a few studies on hydrogen-bonding interactions have illustrated both the promise and difficulty of harnessing this type of secondary interaction.[20,21]

Thus, my group initiated a program to look at the cooperative effects of a transition-metal center and nearby organic moieties capable of proton transfer or hydrogen bonding, using structures schematically illustrated in Scheme 3. Start-



Scheme 3. Schematic of bifunctional substrate activation.

ing from chelate **1**, a polar substrate, such as water (X = OH), could bind reversibly to the single central metal M, while also donating a hydrogen bond or a proton to a pendant basic nitrogen atom, forming **2**. The X–H bond could also be an activated C–H bond in a hydrocarbon, such as an alkyne. Because transition-metal–chelate complexes with five- and six-membered rings are generally the most stable, we wanted to restrict our attention to ligand systems $L(C)_nN$ with one carbon atom (i.e., $n = 1$, not 2 or 3), as we imagined that the resulting four-membered chelates would either not form at all, or be prone to opening by a polar ligand, as shown in Scheme 3, for the desired bifunctional interactions. The presence of the imidazole ring in histidine suggested to us that we examine ligands such as **3**.



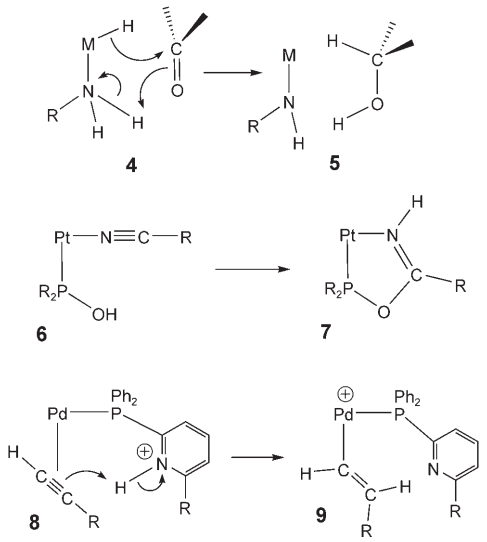
3
a R = H
b R = *t*Bu

Catalysts with two different functional groups, such as **1** or **2** with its metal M and pendant base, are often called bifunctional. Other research groups are investigating such species, and it is worth noting how our systems compare. Bifunctional catalysts can be divided into three types: 1) metal-free organocatalysts, featuring moieties capable of hydrogen bonding or proton transfer or perhaps other interactions (e.g., π stacking); 2) those with a Lewis acidic metal and Brønsted–Lowry base; and 3) those with a transition metal (capable of fundamental organometallic reactions, unlike a simple Lewis acid) and an internal base or acid.

Examples of the first type of organocatalysts,[22–24] are peptides[25,26] or other small molecules with hydrogen-bonding or proton-transferring groups[27] in proximity. The second catalyst type includes Al^{III}, In^{III}, or Ti^{IV} centers held by ligands containing Brønsted–Lowry bases near enough to act on intermediates, but far enough from the metal to prevent

coordination. For examples, see the work of Shibasaki,[28–32] Saa,[33,34] Leckta,[35,36] Snapper and Hoveyda,[37] and Kozlowski.[38] In some systems, even a transition metal (for example, Ru^{II}[39,40]) may act simply as a Lewis acid, not forming metal–carbon bonds.

Finally, the most relevant type of bifunctional catalyst for this article are organometallic complexes. Early examples were provided in 1982 by Kumada[41] (directed attack of nucleophiles on allyl–palladium intermediates) and in 1986 by Ito, Sawamura, and Hayashi (gold-templated aldol reactions).[42] Perhaps now the most famous examples are the transfer hydrogenation catalysts developed extensively by Noyori and co-workers,[43,44] and some related MCp* systems (M = Ru, Rh, Ir; Cp* = η^5-C_5Me_5).[45,46] These complexes (schematically illustrated by **4**; Scheme 4) appear to transfer



Scheme 4. Some key steps proposed in bifunctional organometallic catalysis.

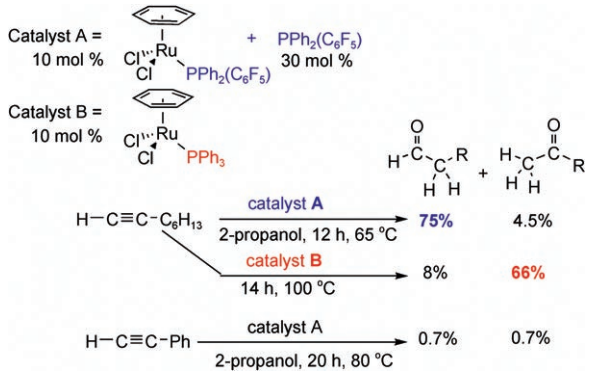
hydrogen by a new, outer-sphere mechanism featuring cooperativity of metal and the N–H moiety of an amine ligand. Other notable examples are 1) the Shvo catalyst recently studied by Casey's group;[47,48] 2) Sigman's alcohol oxidation catalyst, for which he proposes alcohol binding involving proton transfer;[49] 3) nitrile hydration by [Pt(L)$_n$(R$_2$P–OH)] complexes (**6**; Scheme 4),[50–52] which are proposed to act by attack of the pendant hydroxyl on coordinated and activated nitrile functionality (forming **7** as an intermediate); and 4) nitrile hydration by [Ru–H(L)$_n$] complexes, in which the hydride ligand may activate attacking water through hydrogen bonding.[53]

One particularly exciting precedent for some of our research is shown schematically by the proposed conversion of **8** to **9** (Scheme 4). The 2-pyridyl group on a phosphine moiety, as shown in **8**, enables a highly selective alkoxycarbonylation of terminal alkynes, increasing reaction rates by factors of over 1000 times those obtained with only phenyl groups on the ligand.[54–56] Although several roles of the pyridine nitrogen atom and added acid have been discussed, the most recent evidence suggests[55] that a pyridinium moiety may help protonate a π-bound alkyne (in **8**) to form a cationic vinyl complex (**9**).

Thus, there are some very promising literature examples of the importance of proton transfer in organometallic catalysis. A variety of investigations showing the effectiveness of hydrogen bonding or proton transfer are underway in our laboratory; below, the focus is on alkyne hydration.

Anti-Markovnikov Alkyne Hydration

In 1998 our attention was drawn to the first report of catalytic anti-Markonikov hydration of terminal alkynes to give aldehydes (Scheme 5).[57] Prior to this advance, aldehyde for-

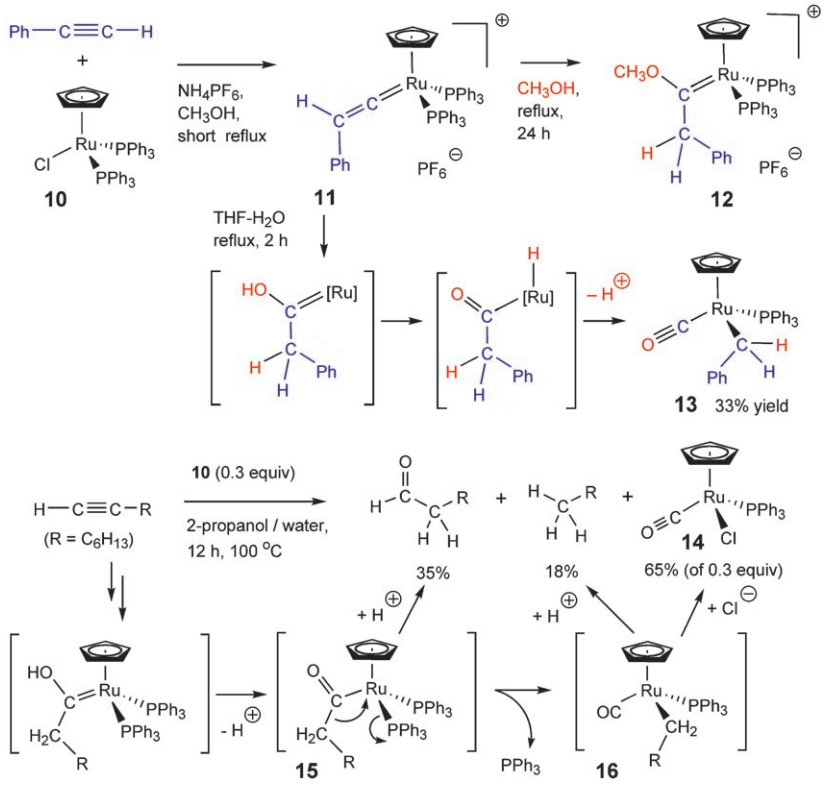


Scheme 5. Phosphine alters regiochemistry of alkyne hydration.

mation from terminal alkynes demanded stoichiometric conversions by using boranes or silanes, followed by oxidation. In addition, previous attempts to catalyze addition of water to terminal alkynes by using transition metals or strong acid resulted in Markovnikov hydration, giving a methyl ketone.

Intriguingly, the Tokunaga and Wakatsuki catalyst could be tuned to give either aldehyde or ketone as the major product, with most ratios on the order of 10:1 or 20:1 in either direction (the highest being 67:1), and the reason for change in regiochemistry was not entirely clear. Moreover, because the best catalyst for aldehyde formation required added phosphine, in order to hydrate a gram of 1-octyne, over 0.5 g of catalyst would be needed. In addition, phenylacetylene gave less than 2% of a 1:1 mixture of aldehyde and ketone.

Tokunaga and Wakatsuki presented evidence that the benzene ligand was soon lost during the catalysis. We reasoned that an anionic Cp ligand (Cp = cyclopentadienyl)-would resist displacement, resulting in a more robust catalyst. A promising literature precedent in this regard was that [Ru(Cp){bis(phosphine)}] species, such as **10** (Scheme 6), react in high yields with terminal alkynes to give vinylidene complexes **11**,[58] key intermediates proposed by Tokunaga and Wakatsuki. Moreover, the carbon atom attached to the



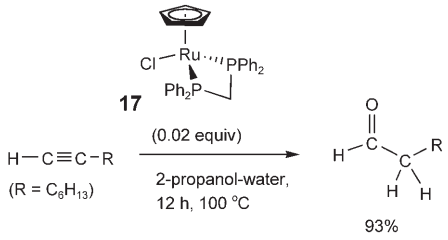
Scheme 6. Elusive alkyne hydration on $[Ru(Cp)(PPh_3)_2]$ complexes.

metal in **11** reacted even with the poor nucleophile methanol, forming a methoxycarbene complex (**12**) in high yield. However, reaction with water was not so simple (or encouraging), affording 33% of the stable complex **13**[58] rather than an aldehyde, though the latter may have escaped detection.

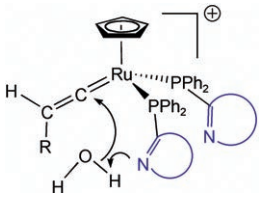
Our initial investigations using 1-hexyne reaffirmed that in acetone containing five equivalents of water, **10** (2 mol%) "catalyzed" the formation of 1% of hexanal, not even one mole of aldehyde per mole of metal complex. While our own investigations were in progress (as described below), in 2001 Suzuki et al. reported[59] that under slightly different conditions, **10** (30 mol%) reacted with 1-octyne to give 35% of aldehyde and 18% of alkane, not quite two turnovers (Scheme 6). Significantly, 65% of the ruthenium was recovered as stable complex **14**, isolation of which (like that of related complex **13** by Bruce and co-workers) suggested that catalyst instability was due to loss of phosphine (**15**, **16**). Two simple and effective remedies applied by the Japanese team were 1) to use smaller, more donating phosphines such as Me_2PPh, since these are less likely to dissociate, or 2) to use chelating phosphines, since in that case if one end of the ligand dissociated it would still be attached at the other end. Indeed,[59] at 100°C, chelating phosphine complex **17** (2 mol%, Scheme 7) catalyzed formation of aldehyde in over 90% yield in many cases, and ketones were not detected. Phenylacetylene was still somewhat problematic, requiring higher catalyst loading (10%). Though this was a significant advance, as shown below, use of ligands capable of proton transfer or hydrogen bonding leads to catalysts that are 90 to 1100 times faster than **17**.

In our own efforts to improve the performance of **10**, adding external base did not improve matters. Nonetheless, we clung to the perhaps naïve hypothesis that positioning a pendant base near the vinylidene system (schematically illustrated in **18**, Scheme 8) would promote formation of a more reactive nucleophile, leading ultimately to alkyne hydration.

Thus, as shown in Scheme 9, two moles of known phosphines **3a**[60] and **19a**[61] were used to displace the acetonitrile ligands from **20**, forming **21** and **22** in high yield. Interestingly, in each product **21** and **22** the same ligand is coordinated in two different environments, one chelating, the other not. Exchange



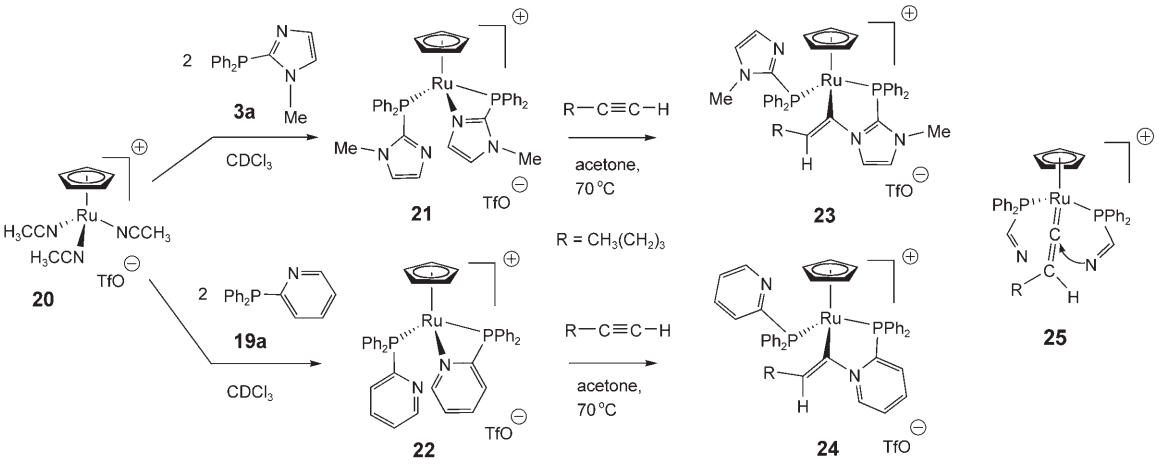
Scheme 7. Phosphine loss problem solved.



Scheme 8. One proposed bifunctional role.

of the two ligand nitrogen atoms and, hence, fluxionality is a process too slow to see in these particular species by normal NMR techniques, but it is a phenomenon seen in our work with other metals. Hundreds of pyridylphosphine complexes have been made and their chemistry reviewed,[62,63] with most of the attention focused on the ability of the P,N ligand to bridge two different metal centers. Fewer imidazolylphosphine complexes have been made,[64] usually for similar purposes, the one important exception being tris(imidazolyl)phosphines used as model ligands for bioinorganic chemistry.[65]

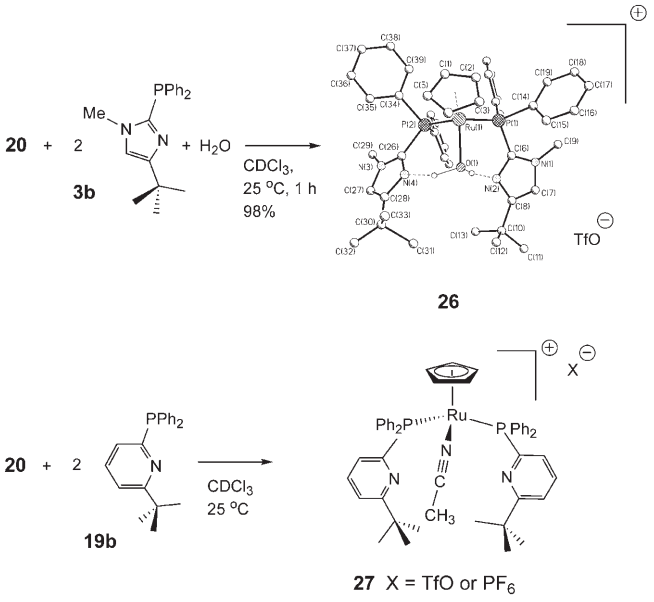
In aqueous acetone, the two complexes reacted with 1-hexyne readily, but hexanal was not formed. Rather, each



Scheme 9. Coordination chemistry and trapping of vinylidene by heterocycle.

complex was converted to a new species (**23**, **24**) incorporating all the atoms of hexyne and of the starting complexes. Though two-dimensional NMR spectroscopy results led to the formulation shown, ultimately X-ray diffraction[66] confirmed that indeed the heterocyclic nitrogen atom had added to C1 of hexyne, presumably at the stage of putative vinylidene complex **25**.

To hinder the direct attack of nitrogen at vinylidene C1 as suggested by **25**, it was decided to add a bulky heterocyclic ring substituent adjacent to the basic nitrogen atom.[67] Thus, reaction of two moles of **3b** (Scheme 10) with **20** in the presence of water (5 equiv) was used to create **26** (98% yield) within an hour. The crystal structure of **26**[67] shows a water molecule in a binding pocket formed by the metal as Lewis acid and the two basic imidazole nitrogen atoms as hydrogen-bond acceptors, a picture conforming to **2** in Scheme 3,



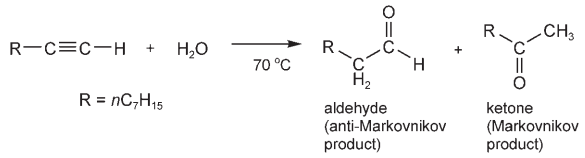
Scheme 10. Formation of alkyne hydration catalysts.

and not unlike the proposed role of Zn^{II} in the carboxypeptidase active site (Scheme 2). Complex **26** (2 mol%) catalyzes aldehyde formation from a variety of terminal alkynes, in the case of 1-nonyne at 90 times the rate of **17**. Alkylacetylenes work the best, whereas phenylacetylene requires additional catalyst (10%). Significantly, for application to fine-chemical synthesis, the acid-sensitive alcohol protecting groups *tert*-butyldimethylsilyl and tetrahydropyranyl are tolerated, showing that reaction conditions are remarkably neutral. Under the conditions employed (5 equiv of water, 70°C, 1 to 2 days), even acids as mild as pyridinium or acetic acid would catalyze removal of the protecting groups tested. Significantly for catalyst design, the presence of a potentially coordinating nitrile group does not alter performance of **26**, probably because the resting state of the catalyst (as determined by NMR spectroscopy of the reaction mixtures) is **26**, in which nitrile is excluded.

Though the crystal structure of **26** validates the model presented by **2** in Scheme 3 and is aesthetically pleasing, it may be that **26** creates too good a binding pocket for water. For one thing, in monitoring reactions by NMR spectroscopy, the resting state of the catalyst appeared to be **26**, not some intermediate in the alkyne hydration. For another, added phosphine (**3b**) did not change the hydration rate, suggesting that both phosphines stayed on the metal and that water dissociation was necessary to open the catalytically active site for alkyne binding. Thus, reduction in hydrogen-bonding strength was attempted by changing the basicity of the heterocyclic nitrogen atom. Related pyridylphosphine **19b**[68] was used to displace two nitriles from **20**, giving **27**.[69] This species proved to be 12.8 times as active as **26**, and 1100 times more active than **17**. With **27**, not only alkylacetylenes but also aryl and electron-rich arylacetylenes were hydrated effectively by only 2 mol% of catalyst. In addition, using 5 mol% of catalyst, alkylacetylenes could be hydrated within two days at room temperature, the first such possibility.[69]

Given these encouraging results, rates and selectivity of aldehyde formation from a terminal alkyne, with catalyst **27**

and without, were experimentally determined (Scheme 11), giving results within the realm of enzymatic performance.

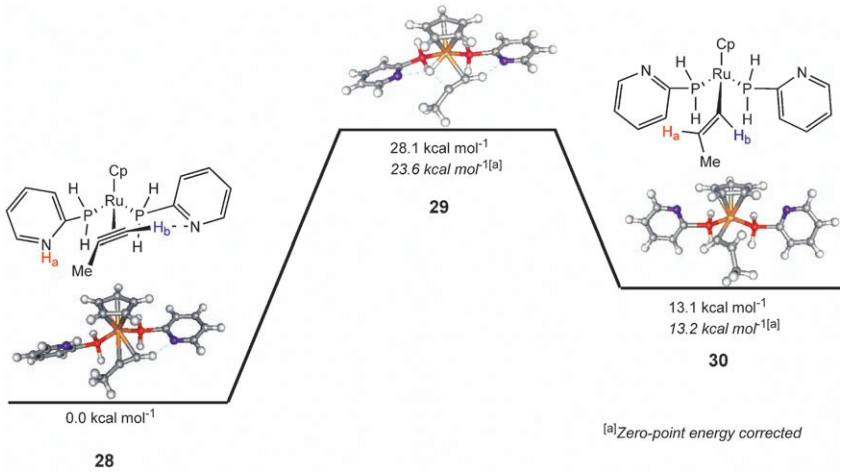


Scheme 11. Enzyme-like rate and selectivity changes: 1) By using protic acid (10 % $HNTf_2$), ratio of aldehyde/ketone of 1:33; 2) by using bifunctional catalyst **27**, ratio $>10000:1$; 3) without catalyst, rate of aldehyde formation $<1\times10^{-10}$ mol h^{-1} (half-life >600000 years!); and 4) with **27**, rate of aldehyde formation 23.8 mol h^{-1} per mol of catalyst—changes in rate and selectivity $>2\times10^{11}$ and >300000, respectively.

Proton Transfer or Hydrogen Bonding?

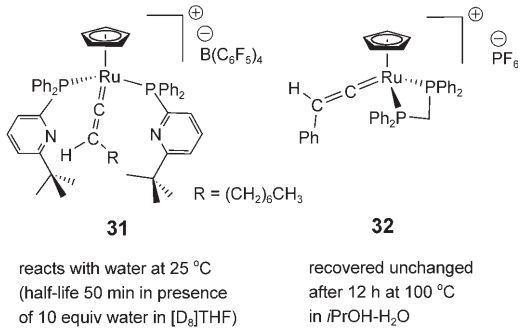
The mechanism of the heterocycle-assisted alkyne hydration is under examination by a combination of experimental and computational methods. There are several mechanistic possibilities (for a review, see reference [70]), but two key steps during which a basic nitrogen may help catalysis are the formation of the vinylidene ligand from alkyne, and subsequently the addition of water to C1 of the vinylidene.

Computational studies[66] of the alkyne-to-vinylidene transformation suggest bifunctional activation of the alkyne, as seen in Scheme 12. Following the important revelations



Scheme 12. Calculated structures in the reaction of propyne on $CpRu[H_2P(C_5H_4N)]_2^+$.

from Tokunaga et al.,[70] protonation of bound propyne by H_a in **28** was considered. As H_a migrates, its movement appears to be assisted by the metal in the transition state (**29**), which features a three-point interaction between pyridine N, Ru, and alkyne carbon to which H_a is migrating in forming vinyl derivative **30**. The role of the hydrogen-bonding interaction in **28** between the terminal alkyne hydrogen H_b and the other pyridine is also under scrutiny. On the experimental side, one highlight of the work in progress includes the recent isolation of vinylidene complex **31** and the observation that it is sensitive to water at ambient temperatures (Scheme 13). This contrasts sharply with the literature



Scheme 13. Contrasting reactivity of vinylidene complexes derived from catalysts **27** and **17**.

report[70] that vinylidene complex **32** was recovered unchanged after 12 h at 100 °C in isopropanol/water! In short, efforts continue to answer the question posed above.

Conclusion

Regardless of mechanistic effect, polar pendant groups suitably placed near a transition-metal center show great promise for activation and functionalization of nonpolar substrates. New mechanisms that use both the capabilities of the transition metal to change its d-electron count and the movement of protons during the catalytic cycle are expected to open further possibilities in catalysis.

Acknowledgements

I am indebted to a dedicated group of present and past co-workers, in particular (now Dr.) Daniel Lev, who did much of the experimental work and all of the computational work on this project. Funding from the U.S. National Science Foundation (CHE-0415783) is also acknowledged.

[1] J. M. Thomas, *Angew. Chem.* **1994**, *106*, 963–989; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 913–937.
[2] *Technology Vision 2020*, The Chemical Industry Vision 2020 Technology Partnership, **1996**.
[3] B. R. James, *Homogeneous Hydrogenation*, Wiley, New York, **1973**.
[4] R. M. Bullock, *Chem. Eur. J.* **2004**, *10*, 2366–2374.
[5] R. Noyori, *Angew. Chem.* **2002**, *114*, 2108–2123; *Angew. Chem. Int. Ed.* **2002**, *41*, 2008–2022.

[6] J. F. Young, J. A. Osborn, F. H. Jardine, G. Wilkinson, *Chem. Commun.* **1965**, 131–132.
[7] W. S. Knowles, *Angew. Chem.* **2002**, *114*, 2096–2107; *Angew. Chem. Int. Ed.* **2002**, *41*, 1998–2007.
[8] R. H. Crabtree, M. W. Davis, *Organometallics* **1983**, *2*, 681–682.
[9] A. G. Schultz, P. J. McCloskey, *J. Org. Chem.* **1985**, *50*, 5905–5907.
[10] T. E. Creighton, *Proteins: Structures and Molecular Properties*, W. H. Freeman, New York, **1993**, pp. 418–434.
[11] A. Radzicka, R. Wolfenden, *J. Am. Chem. Soc.* **1996**, *118*, 6105–6109.
[12] R. A. R. Bryant, D. E. Hansen, *J. Am. Chem. Soc.* **1996**, *118*, 5498–5499.
[13] G. Helmchen, H. Steinhagen, *Angew. Chem.* **1996**, *108*, 2489–2492; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2339–2342.
[14] E. K. van den Beuken, B. L. Feringa, *Tetrahedron* **1998**, *54*, 12985–13011.
[15] G. J. Rowlands, *Tetrahedron* **2001**, *57*, 1865–1882.
[16] For examples of other secondary interactions used, see a) C. R. Landis, R. A. Sawyer, E. Somsook, *Organometallics* **2000**, *19*, 994–1000; b) H. Brunner, R. Störiko, F. Rominger, *Eur. J. Inorg. Chem.* **1998**, 771–781; c) G. B. Jones, B. J. Chapman, *Synthesis* **1995**, 475–497.
[17] L. Brammer, *Dalton Trans.* **2003**, 3145–3157.
[18] D. Braga, F. Grepioni, E. Tedesco, K. Biradha, G. R. Desiraju, *Organometallics* **1997**, *16*, 1846–1856.
[19] R. H. Crabtree, P. E. M. Siegbahn, O. Eisenstein, A. L. Rheingold, T. F. Koetzle, *Acc. Chem. Res.* **1996**, *29*, 348–354.
[20] A. Börner, *Eur. J. Inorg. Chem.* **2001**, 327–337.
[21] I. Yamada, K. Fukui, Y. Aoki, S. Ikeda, M. Yamaguchi, T. Yamagishi, *J. Organomet. Chem.* **1997**, *539*, 115–120.
[22] P. I. Dalko, L. Moisan, *Angew. Chem.* **2001**, *113*, 3840–3864; *Angew. Chem. Int. Ed.* **2001**, *40*, 3726–3748.
[23] E. R. Jarvo, S. J. Miller, *Tetrahedron* **2002**, *58*, 2481–2495.
[24] P. R. Schreiner, *Chem. Soc. Rev.* **2003**, *32*, 289–296.
[25] E. R. Jarvo, G. T. Copeland, N. Papaioannou, P. J. Bonitatebus, Jr., S. J. Miller, *J. Am. Chem. Soc.* **1999**, *121*, 11638–11643.
[26] M. S. Sigman, P. Vachal, E. N. Jacobsen, *Angew. Chem.* **2000**, *112*, 1336–1338; *Angew. Chem. Int. Ed.* **2000**, *39*, 1279–1281.
[27] T. Okino, Y. Hoashi, Y. Takemoto, *J. Am. Chem. Soc.* **2003**, *125*, 12672–12673.
[28] Y. Hamashima, D. Sawada, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **1999**, *121*, 2641–2642.
[29] K. Funabashi, H. Ratni, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2001**, *123*, 10784–10785.
[30] M. Shibasaki, H. Sasai, T. Arai, *Angew. Chem.* **1997**, *109*, 1290–1310; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1236–1256.
[31] H. Groger, *Chem. Eur. J.* **2001**, *7*, 5246–5251.
[32] M. Kanai, *Yakugaku Zasshi* **2001**, *121*, 949–960.
[33] J. Casas, C. Najera, J. M. Sansano, J. M. Saa, *Org. Lett.* **2002**, *4*, 2589–2592.
[34] J. Casas, C. Najera, J. M. Sansano, J. M. Saa, *Tetrahedron* **2004**, *60*, 10487–10496.
[35] S. France, H. Wack, A. M. Hafez, A. E. Taggi, D. R. Witsil, T. Lectka, *Org. Lett.* **2002**, *4*, 1603–1605.
[36] S. France, M. H. Shah, A. Weatherwax, H. Wack, J. P. Roth, T. Lectka, *J. Am. Chem. Soc.* **2005**, *127*, 1206–1215.
[37] N. S. Josephsohn, K. W. Kuntz, M. L. Snapper, A. H. Hoveyda, *J. Am. Chem. Soc.* **2001**, *123*, 11594–11599.
[38] E. F. DiMauro, M. C. Kozlowski, *J. Am. Chem. Soc.* **2002**, *124*, 12668–12669.
[39] C. S. Yi, S. Y. Yun, Z. He, *Organometallics* **2003**, *22*, 3031–3033.
[40] N. Kumagai, S. Matsunaga, M. Shibasaki, *J. Am. Chem. Soc.* **2004**, *126*, 13632–13633.
[41] T. Hayashi, K. Kanehira, H. Tsuchiya, M. Kumada, *J. Chem. Soc. Chem. Commun.* **1982**, 1162–1164.
[42] M. Sawamura, Y. Ito, *Chem. Rev.* **1992**, *92*, 857–871.
[43] R. Noyori, M. Yamakawa, S. Hashiguchi, *J. Org. Chem.* **2001**, *66*, 7931–7944.
[44] R. Noyori, T. Ohkuma, *Angew. Chem.* **2001**, *113*, 40–75; *Angew. Chem. Int. Ed.* **2001**, *40*, 40–73.
[45] T. Suzuki, K. Morita, M. Tsuchida, K. Hiroi, *Org. Lett.* **2002**, *4*, 2361–2363.
[46] M. Ito, A. Osaku, S. Kitahara, M. Hirakawa, T. Ikariya, *Tetrahedron Lett.* **2003**, *44*, 7521–7523.
[47] C. P. Casey, S. W. Singer, D. R. Powell, R. K. Hayashi, M. Kavana, *J. Am. Chem. Soc.* **2001**, *123*, 1090–1100.
[48] C. P. Casey, J. B. Johnson, S. W. Singer, Q. Cui, *J. Am. Chem. Soc.* **2005**, *127*, 3100–3109.
[49] a) D. R. Jensen, M. J. Schultz, J. A. Mueller, M. S. Sigman, *Angew. Chem.* **2003**, *115*, 3940–3943; *Angew. Chem. Int. Ed.* **2003**, *42*, 3810–3813; b) J. A. Mueller, C. P. Goller, M. S. Sigman, *J. Am. Chem. Soc.* **2004**, *126*, 9724–9734.
[50] T. Ghaffar, A. W. Parkins, *Tetrahedron Lett.* **1995**, *36*, 8657–8660.
[51] T. Ghaffar, A. W. Parkins, *J. Mol. Catal. A* **2000**, *160*, 249–261.
[52] X.-b. Jiang, A. J. Minnaard, B. L. Feringa, J. G. De Vries, *J. Org. Chem.* **2004**, *69*, 2327–2331.
[53] W. K. Fung, X. Huang, M. L. Man, S. M. Ng, M. Y. Hung, Z. Lin, C. P. Lau, *J. Am. Chem. Soc.* **2003**, *125*, 11539–11544.
[54] E. Drent, P. Arnoldy, P. H. M. Budzelaar, *J. Organomet. Chem.* **1994**, *475*, 57–63.
[55] A. Scrivanti, V. Beghetto, E. Campagna, M. Zanato, U. Matteoli, *Organometallics* **1998**, *17*, 630–635.
[56] A. Dervisi, P. G. Edwards, P. D. Newman, R. P. Tooze, *J. Chem. Soc. Dalton Trans.* **2000**, 523–528.
[57] M. Tokunaga, Y. Wakatsuki, *Angew. Chem.* **1998**, *110*, 3024–3027; *Angew. Chem. Int. Ed.* **1998**, *37*, 2867–2869.
[58] M. I. Bruce, A. G. Swincer, *Aust. J. Chem.* **1980**, *33*, 1471–1483.
[59] T. Suzuki, M. Tokunaga, Y. Wakatsuki, *Org. Lett.* **2001**, *3*, 735–737.
[60] M. A. Jalil, T. Yamada, S. Fujinami, T. Honjo, H. Nishikawa, *Polyhedron* **2001**, *20*, 627–633.
[61] F. G. Mann, J. Watson, *J. Org. Chem.* **1948**, *13*, 502–531.
[62] G. R. Newkome, *Chem. Rev.* **1993**, *93*, 2067–2089.
[63] Z.-Z. Zhang, H. Cheng, *Coord. Chem. Rev.* **1996**, *147*, 1–39.
[64] Examples: a) A. Burini, B. R. Pietroni, R. Galassi, G. Valle, S. Calogero, *Inorg. Chim. Acta* **1995**, *229*, 299–305; b) M. A. Jalil, T. Yamada, S. Fujinami, T. Honjo, H. Nishikawa, *Polyhedron* **2001**, *20*, 627–633; c) C. Tejel, M. A. Ciriano, R. Bravi, L. A. Oro, C. Graiff, R. Galassi, A. Burini, *Inorg. Chim. Acta* **2003**, *347*, 129–136; d) G. Espino, F. A. Jalon, M. Maestro, B. R. Manzano, M. Perez-Manrique, A. C. Bacigalupe, *Eur. J. Inorg. Chem.* **2004**, 2542–2552.
[65] D. A. Lev, L. Zakharov, J. A. Golen, A. L. Rheingold, unpublished results.
[66] Examples: a) R. S. Brown, M. Zamkanei, J. L. Cocho, *J. Am. Chem. Soc.* **1984**, *106*, 5222–5228; b) H. Slebocka-Tilk, J. L. Cocho, Z. Frackman, R. S. Brown, *J. Am. Chem. Soc.* **1984**, *106*, 2421–2431; c) W. E. Allen, T. N. Sorrell, *Inorg. Chem.* **1997**, *36*, 1732–1734; d) W. Kläui, C. Piefer, G. Rheinwald, H. Lang, *Eur. J. Inorg. Chem.* **2000**, 1549–1555; e) C. Kimblin, V. J. Murphy, T. Hascall, B. M. Bridgewater, J. B. Bonanno, G. Parkin, *Inorg. Chem.* **2000**, *39*, 967–974.
[67] D. B. Grotjahn, C. D. Incarvito, A. L. Rheingold, *Angew. Chem.* **2001**, *113*, 4002–4005; *Angew. Chem. Int. Ed.* **2001**, *40*, 3884–3887.
[68] J. Baur, H. Jacobsen, P. Burger, G. Artus, H. Berke, L. Dahlenburg, *Eur. J. Inorg. Chem.* **2000**, 1411–1422.
[69] D. B. Grotjahn, D. A. Lev, *J. Am. Chem. Soc.* **2004**, *126*, 12232–12233.
[70] M. Tokunaga, T. Suzuki, N. Koga, T. Fukushima, A. Horiuchi, Y. Wakatsuki, *J. Am. Chem. Soc.* **2001**, *123*, 11917–11924.

Published online: August 5, 2005

