mixture. After each addition of the $AlPO_4$-5 synthesis mixture, the container was stirred for several minutes before making visual observations. The minimum amount of $AlPO_4$-5 synthesis mixture required to form the microemulsion was determined by the observation of a transparent single-phase. The maximum solubility of $AlPO_4$-5 synthesis mixture in the microemulsion was defined by the onset of visual turbidity. The ratio of butanol to surfactant was varied from 2:1 to 1:2. The single-phase microemulsion did not form in the absence of butanol.

Hydrothermal synthesis: Autoclave synthesis was counducted in a teflon-lined pressure vessel (Parr, model 4744) wrapped in heating tape and controlled to a temperature of 180 °C for 6 h. The reactor contents were stirred continuously using a magnetically coupled teflon stir bar. Microwave synthesis was conducted in teflon acid digestion vessels in a CEM MDS-2000 oven. The vessels were heated to 180 °C for 17 min without stirring.

Powder X-ray diffraction spectra were collected by using a Scintag XDS2000 diffractometer using an accelerating volatge of 45 kV and intensity of 40 mA. The diffraction pattern was collected from an angle 2Θ of 5 to 50°, using a step size of 0.02° and a collection time at each step of 3 s. Scanning electron micrographs were obtained by using a JEOL 6300FX high-resolution scanning electron microscope operating at an accelerating voltage of 1.0 kV.

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Biomimetic NAD^+ Models for Tandem Cofactor Regeneration, Horse Liver Alcohol Dehydrogenase Recognition of 1,4-NADH Derivatives, and Chiral Synthesis**

H. Christine Lo and Richard H. Fish*

In memory of Dr. E. Steckhan

The biocatalysis discipline has the potential to generate important chiral organic compounds, by the use of enzymes, usually in the presence of critical cofactors.[1, 2] Therefore, practical methods for the regeneration of the coenzyme 1,4-NADH are significant in biocatalysis.[3–5] In this manner, a variety of transition metal hydrides have been evaluated as catalysts for the regioselective reduction of NAD^+ and NAD^+ models to the corresponding 1,4-NADH derivatives to develop faster rates and a more economical regeneration process.[6–9] In the most significant example, Steckhan et al. described the in situ generation of $[Cp^*Rh(bpy)(H)]^+$ ($Cp^* = \eta^5$-C_5Me_5, bpy = 2,2′-bipyridyl) for the regiospecific reduction of natural NAD^+ to 1,4-NADH,[7] and then demonstrated the cofactor regeneration process in enzymatic chiral reduction reactions with horse liver alcohol dehydrogenase (HLDAH).[10–12]

More importantly, we recently reported the source of this unusually high regioselectivity for 1,4-NADH and other mechanistic aspects with a model NAD^+ compound, 1-benzylnicotinamide triflate (**1**; Scheme 1). The reaction in H_2O/THF (1:1) used $[Cp^*Rh(bpy)(H_2O)](OTf)_2$ (**2**) as the catalyst precursor, and sodium formate as the hydride source to provide exclusively the kinetic product, 1-benzyl-1,4-dihydronicotinamide (**3**).[13]

Furthermore, we also recently used an aqueous NAD^+ model, β-nicotinamide-5′-ribose methyl phosphate (**4**) and demonstrated its similar regioselective reduction with $[Cp^*Rh(bpy)(H)]^+$, formed in situ, to give the corresponding 1,4-dihydronicotinamide-5′-ribose methyl phosphate (**5**) at pH 6.5.[14] NAD^+ model **4** bears a structural resemblance to NAD^+ (a monoribose phosphate moiety, but with no pyrophosphate or adenosine substituents), while NAD^+ biomimetic **1** has a simple 1-benzyl group instead of the ribose, pyrophosphate, and adenosine groups.

The initial rates (r_i) of the regioselective reduction of both **1** in H_2O/THF (4:1) and **4** in H_2O at pH 6.5 with $[Cp^*Rh(bpy)(H)]^+$ (generated in situ) to give their corre-

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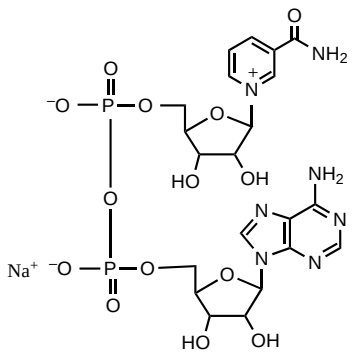


NAD^+

sponding 1,4-dihydro analogues (**3** and **5**) were comparable to that of NAD^+ in H_2O at pH 6.5 (Scheme 1; turnover frequency (TOF): 20 h^{-1}).[14] Therefore, we decided to use both **1** and **4** as biomimetics of NAD^+ in chiral reduction reactions, in conjunction with the above-mentioned cofactor regeneration method.[13, 14] Moreover, recent studies with other NAD^+ biomimetics by Lowe and co-workers showed that primary alcohols were oxidized to aldehydes and that 1,4-NADH biomimetic was produced. The reverse reaction, that is, the reduction of aldehydes to alcohols, along with NAD^+ biomimetic production, was not observed.[15–17]

Two questions arose: What is the role of each substituent on the 1,4-dihydronicotinamide nucleus, including ribose, pyrophosphate, and adenosine groups? Will HLADH enzyme recognition at the binding site for the cofactor prevail to provide chiral reduction products with the most important structural feature still present in our biomimetic 1,4-NADH models: the 1,4-dihydronicotinamide nucleus?[18–21]

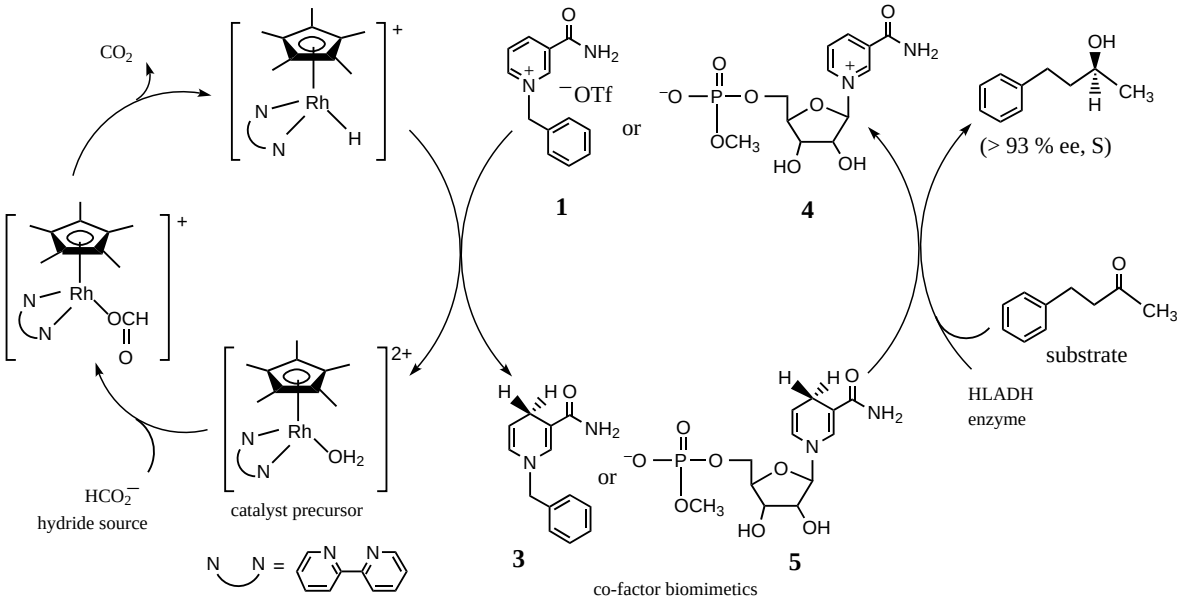
The preliminary tandem cofactor regeneration and chiral synthesis experiments with substrates **6**—**10** (Table 1) and NAD^+ biomimetics **1** and **4**, with NAD^+ as a comparison, provided quite startling and dramatic results. For example, in the presence of HLADH, **6** was reduced to give (*S*)-**11** (>93% *ee*; TOF ~30 d^{-1}). Both NAD^+ models **1** and **4** gave results similar to those with NAD^+ (Table 1). Clearly, all that is necessary for HLADH recognition of the 1,4-NADH biomimetics **3** and **5** is the 1,4-dihydronicotinamide moiety. The possible binding role of 1-benzyl and of ribose-5′-methyl phosphate in the hydrophobic pocket of HLADH does not appear to compromise the transfer of hydride to the ketone substrate to provide chiral alcohol (Scheme 1).

A structure–reactivity study of a variety of ketone substrates (Table 1) further showed that benzyl methyl ketone (**7**) gave (*S*)-**12** (>99% *ee*, TOF 18 d^{-1}), whereas benzophenone (**8**) was extremely slow (TOF, 2 d^{-1}) in providing chiral (*S*)-**13** (>93% *ee*) after 24 h. Alkyl ketone **9** provided predominantly (*S*)-**14** (85% ee), similar to the results

Table 1. Enzymatic reductions of prochiral ketones with NAD^+ models **1** and **4**: turnover frequencies and *ee* values.[a,b]

substrate	product	% yield	TOF [d^{-1}]	*ee* [%, S]
$PhCH_2CH_2C(=O)CH_3$ **6**	$PhCH_2CH_2C^*(OH)H-CH_3$ **11**	90(91)	30(31)	93(93)
$PhCH_2C(=O)CH_3$ **7**	$PhCH_2C^*(OH)H-CH_3$ **12**	55(59)	18(19)	>99(99)
$PhC(=O)CH_3$ **8**	$Ph-C^*(OH)H-CH_3$ **13**	5(5)	4(4)	>96(96)
$CH_3CH_2CH_2C(=O)CH_3$ **9**	$H_3C-CH_2-C^*(OH)H-CH_3$ **14**	41(59)	14(20)	85(85)[c]

[a] Models **1** and **4** provided similar results within experimental error (<2%). The results obtained with NAD^+ are given in parenthesis. [b] The *ee* values were determined by means of GC analysis with a modified β-cyclodextrin capillary column. [c] Based on the analysis of carbamate diastereomers with an optically pure isocyanate derivative.



Scheme 1. Plausible catalytic reduction cycle for the synthesis of 1,4-NADH biomimetics, **3** or **5**, followed by a catalytic cycle for chiral alcohol synthesis from ketone substrates with the enzyme, HLADH.

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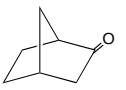
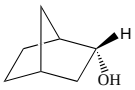
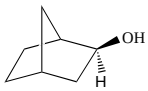
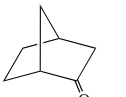
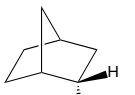
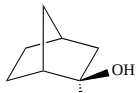
obtained with NAD^+. This may demonstrate that the binding site for this type of alkyl ketone is not as rigid as the binding site for phenethyl ketone to engender higher chirality to the alcohol product.

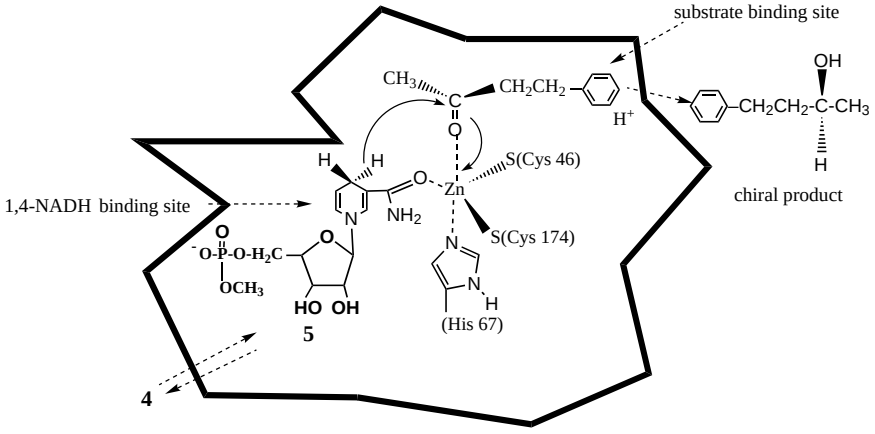
Alternatively, the enantiomers of bulky norcamphor (**10**) were reduced at different rates and also provided a different diastereomeric mixture of predominantly *endo* chiral alcohols. As shown in Table 2, one enantiomer of **10** gave an approximately equal mixture of the *exo* and *endo* alcohols, whereas the other gave exclusively the *endo* alcohol with no *exo* alcohol detected.

Table 2. Enzymatic conversion of racemic norcamphor: turnover frequency (TOF) and yield with NAD^+ models **1** and **4**.[a]

Substrate	Product		Yield [%]	TOF [d^{-1}]
			86 (94)	28 (29)
(+)-(1*S*,4*R*)-**10** 0.5 equiv	(+)-(1*S*,2*R*,4*R*) 0.45 (0.48)	(+)-(1*S*,2*R*,4*R*) 0.0 (0.0)		
				
(−)-(1*R*,4*S*)-**10** 0.5 equiv	(−)-(1*R*,2*S*,4*S*) 0.21 (0.25)	(−)-(1*R*,2*R*,4*S*) 0.20 (0.21)		

[a] The results obtained with NAD^+ are given in parenthesis.

Interestingly, the hydride transfer pathway from 1,4-NADH to the HLADH-bound ketone is still very controversial; various mechanisms have been proposed, but none appear very satisfactory.[22] The previously formulated results indicated that the initial binding process of natural 1,4-NADH occurs in proximity to the Zn^{2+} center of HLADH, and the Zn^{2+}-bound substrate.[23, 24] In a manner similar to that of the $[Cp^*Rh(bpy)H]^+$ binding of biomimetic **1** for the regioselective production of **3**,[13, 14] we also envision the possibility that the carbonyl function of the amide group of 1,4-NADH, and that of biomimetics **3** or **5**, might weakly bind to the Zn^{2+} center to stabilize this hydride-transfer process (Scheme 2).



Scheme 2. Postulated active-site model for HLADH with 1,4-NADH biomimetic **5** as hydride source and phenethyl methyl ketone (**6**) as substrate.

This possible Zn^{2+}-binding process of the cofactor during the transfer of hydride from **5** to the *Re* face of the carbonyl group could also conceivably add stability to the microscopic reverse reaction, that is, hydride transfer from a specific C–H of RCH_2OZn to **4**, to give a C=O product and **5**. We have, in fact, shown that the reverse reaction, (*S*)-**14** to **9** occurs with NAD^+ biomimetic **4**, whereas the *R* enantiomer was found to be extremely slow.

This potential binding regime allows the Zn^{2+} metal center to become 4- or 5-coordinate during the 1,4-NADH hydride-transfer process in the presence of the carbonyl substrate. Recently, Sagi and co-workers[25] have strengthened the concept of the Zn^{2+} center being a template for much of the ADH reactivity. They demonstrated with a thermophilic ADH enzyme (TbADH) that the Zn^{2+} center exhibits a pentacoordinate structure, and developed an active-site model that reflected their results with Asp 150, His 59, Glu 60, Cys 37, and DMSO as the surrogate substrate, coordinated to the Zn^{2+}.[25]

In conclusion, we have demonstrated that biomimetic NAD^+ models, which were structurally modified to retain the nicotinamide nucleus as NAD^+ and either one similar substituent, the ribose-5′-phosphate group, or none, the 1-benzyl group, can be converted regioselectively into their 1,4-dihydronicotinamide analogues. We have clearly shown for the first time, to the best of our knowledge, that these 1,4-NADH biomimetics are recognized by the HLADH cofactor binding site in the chiral synthesis of aryl/alkyl-substituted alcohols. Although the economic benefits of this discovery can not be fully evaluated at this time for biocatalytic applications, it is clear from the presented results, and previous observations,[15–17] that some structural features of 1,4-NADH need not be present for enzyme recognition and for the synthesis of chiral organic compounds. We hope that our results pave the way for the possible utilization of NAD^+ models such as **1** and **4** in a variety of biocatalytic processes of industrial importance; model **1** and other potential analogues are more stable under conditions that might cause the NAD^+ to be hydrolytically compromised.[26, 27]

Experimental Section

General Procedure (Reduction): $[Cp^*Rh(bpy)(H_2O)]OTf_2$ (1.9 mg, 2.61×10^{-3} mmol), sodium formate (17.8 mg, 261.69×10^{-3} mmol), NAD^+ (or NAD^+ models **1** or **4**) (8.1 mg, 11.23×10^{-3} mmol), and HLADH (10 units) were placed in a 10-mL Schlenk flask, and Schlenk techniques were used to deoxygenate the solid mixture. Under positive argon pressure, potassium phosphate buffer (5 mL, 100 mM, pH 7.02, deoxygenated) and the carbonyl substrate (83.58×10^{-3} mmol, deoxygenated) were added successively through a syringe. The reaction flask was immediately capped securely with a glass stopper and shaken by using a shaker in a 30 °C water bath. The reaction was monitored by means of GC, equipped with a β-cyclodextrin column (Supelco, β-DEX-225). The products were identified by comparing the retention time with authentic chiral samples, and were confirmed by GC-MS. The *ee* values of the products were directly determined by calculating their relative areas from the chromatograms. The progress of the reaction was obtained by mixing the reaction

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aliquot with an internal standard (cyclohexanol in phosphate buffer), and then calibrating the measured relative area in the chromatogram with their corresponding response factors. The reaction was monitored for 24 h.

Control Experiments: No chiral alcohol product was formed in the absence of the HLADH enzyme, while no ketone was reduced to alcohol in the presence of the model cofactors **1** and **4**. The latter result shows that **1** and **4** preferentially bind to the Cp*Rh center in the presence of the ketone, and they are reduced regioselectively to their 1,4-NADH derivatives **3** and **5**, all in the absence of HLADH.

General Procedure (Oxidation): NAD^+ (83.58×10^{-3} mmol) or NAD^+ models **1** or **4** and HLADH (10 units) were placed in a 10-mL Schlenk flask, and Schlenk techniques were used to deoxygenate the solid mixture. Under positive argon pressure, potassium phosphate buffer (5 mL, 100 mM, pH 7.04, deoxygenated) and (*S*)-2-pentanol (83.58×10^{-3} mmol) were added successively through a syringe. The reaction flask was immediately capped securely with a glass stopper and shaken by using a shaker at room temperature. The progress of the reaction was monitored by means of GC, and the product, 2-pentanone, was identified by comparing the retention time with that of an authentic sample. The oxidation of (*R*)-2-pentanol was also tested under the same conditions, and its reaction rate was found to be much slower than that of (*S*)-2-pentanol. The relative rates of (*S*)- and (*R*)-2-pentanol in the first 24 hr were ~4:1. Additionally, the reactions were found to reach equilibrium after ~60 h (in the case of (*S*)-2-pentanol), at which point both 2-pentanol and 2-pentanone were present in the reaction mixture in a ratio of ~40:60. The same procedure described in the example with NAD^+ was followed with the water soluble model **4**. Both racemic 2-pentanol and (*S*)-2-pentanol were tested, and similar results were obtained as stated in the case of NAD^+, except that the reaction rate became slower after 24 h.

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Transfer of Chiral Information through Achiral Ion Recognition by a Novel Pseudocrown Ether with a Binaphthyl Moiety

Tatsuya Nabeshima,* Akihiro Hashiguchi, Toshiyuki Saiki, and Shigehisa Akine

Chiral products obtained from metabolic processes are often used as reactants for subsequent asymmetric reactions in different chiral environments.[1] Not only chemical reactions but also physical events, such as the selective transport of chiral substrates, require chiral communication between the molecules engaged in the chiral process. Thus, transfer, transduction, modulation, and amplification of chiral information are essential issues for all chiral phenomena. These processes, however, are usually regulated by chiral molecules. Hence, the regulation of such chiral events by an achiral species is extremely fascinating and important.

Allostery and feedback are good examples of the transfer of molecular information, and they regulate many biological events that are linked to each other.[2] These regulating processes play an important role in controlling the function of proteins and they are effective for triggering a certain cascade of reactions in which molecular information is transferred and/or amplified. Many artificial allosteric receptors have recently been reported in which their function is regulated by a single effector, although multistep response to several different stimuli should be very useful for constructing cascade systems[3] and molecular logic devices.[4, 5]

Here we report that podand **1**[6] dually responds to external stimuli, its conversion to a pseudocrown ether complex $[Cu^I(\mathbf{1})]$, and the transfer of chiral information in $[Cu^I(\mathbf{1})]$ by achiral guests, namely alkali metal ions. Precursor

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