CHEMISTRY LETTERS, pp. 1651-1654, 1987.

Photosensitized Hydride Transfer. Highly Regioselective 1,4-Photoreduction of NAD(P)$^+$ Models under Visible Light with an Organometallic Rhodium(III) Porphyrin as Sensitizer[1)]

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An organometallic acetyl-Rh complex of octaethylporphyrin catalyzes under the visible light the photoreduction of 1-benzylnicotinamide (BNA$^+$) or 1-benzyl-3-acetylpyridinium ion (BAP$^+$) as NAD(P)$^+$ model with tetraphenylborate as a reductant and an alcohol as a proton source to give the corresponding 1,4-dihydro derivative (BNAH or BAPH) as the sole reduction product and biphenyl as the oxidation product of $B(C_6H_5)_4^-$.

Redox photosensitization, especially in relation to artificial photosynthesis, is a rapidly growing area.[2)] Metal complexes (M), such as chlorophylls, Zn-porphyrins, and $[Ru(bpy)_3]^{2+}$ (bpy; 2,2'-bipyridine), usually undergo photo-induced one-electron (1e) transfer (Eq. 1, where M is either D (donor) or A (acceptor)),[2)] and directly catalyze 1e redox reactions by radical mechanisms.[3)]

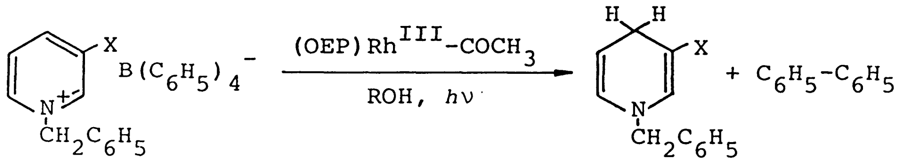
$$D + A \xrightarrow{h\nu} D^{\overset{+}{\cdot}} + A^{\overset{-}{\cdot}} \qquad (1)$$

Heterogeneous colloidal catalysts have been used as electron pools to link up 1e photosensitization processes and multi-electron reactions at the redox termini.[4)] On the other hand, we have been trying to develop new photosystems involving two-electron (2e) or equivalent hydride transfer which is photosensitized by homogeneous metal complexes. Now, we wish to report that a Rh(III) porphyrin catalyzes a number of novel photochemical hydride-transfer reactions under the visible light.

Photosynthetic electron transport results in the reduction of nicotinamide coenzyme NADP$^+$ to NADPH. An organometallic acetyl-Rh(III) complex of octaethylporphyrin, $(OEP)Rh^{III}-COCH_3$,[5)] was found to catalyze the photoreduction of 1-benzylnicotinamide (BNA$^+$) and the 1-benzyl-3-acetylpyridinium ion (BAP$^+$) as NAD(P)$^+$ model to the corresponding 1,4-dihydro derivatives (BNAH and BAPH) with tetraphenylborate ($B(C_6H_5)_4^-$) as a reductant.[6)] This ion is known to undergo 2e oxidation with a variety of oxidants, giving rise to biphenyl according to Eq. 2.[7)] Thus, irradiation of a degassed solution of $(OEP)Rh^{III}-COCH_3$ (1.1×10^{-6} mol) and $BNA^+B(C_6H_5)_4^-$ (2.2×10^{-5} mol)[8)] in $C_6H_6-CH_3CN-(CH_3)_2CHOH$ (5:2:5 v/v) with a 500-W xenon lamp (>500 nm) at 15 °C for 9 h afforded BNAH (1.5×10^{-5} mol; yield, 940 and 68% based on the Rh complex and the BNA salt used, respectively)

$$B(C_6H_5)_4^- \longrightarrow B(C_6H_5)_2^+ + C_6H_5-C_6H_5 + 2e \qquad (2)$$

and C_6H_5-C_6H_5 (1.5 x 10^{-5} mol) (Eq. 3).[9] The Rh complex was recovered as unchanged. Neither the 1,6-dihydro derivative nor the nicotinamide dimer which



(3)

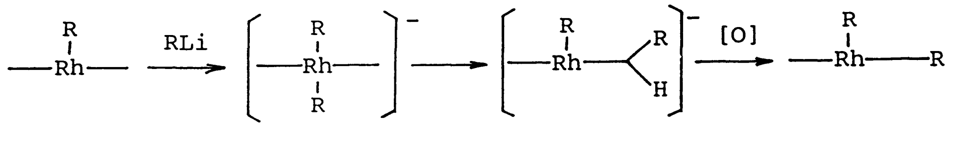
$BNA^+B(C_6H_5)_4^-$: X = $CONH_2$
$BAP^+B(C_6H_5)_4^-$: X = $COCH_3$

BNAH : X = $CONH_2$
BAPH : X = $COCH_3$

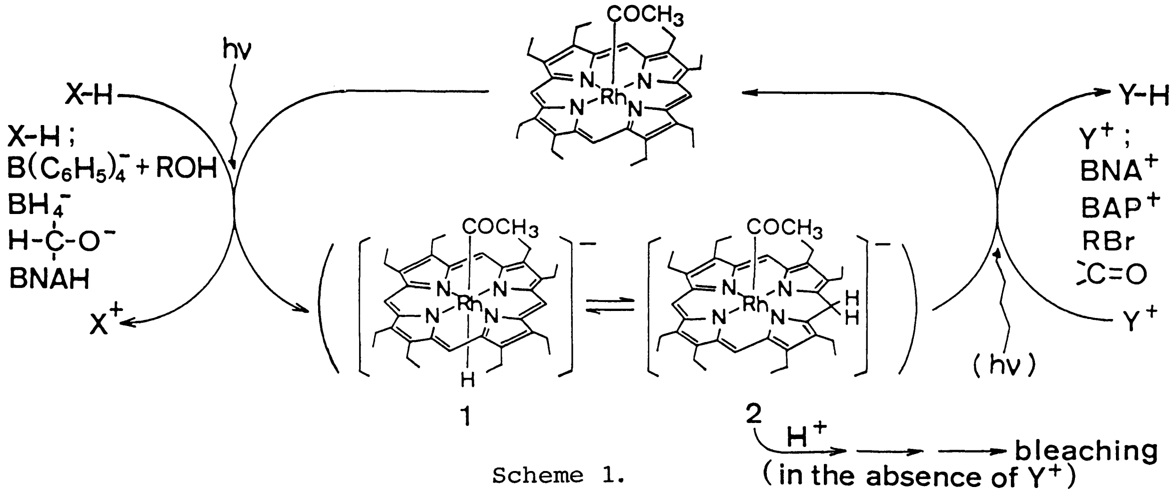
might result from 1e reduction of BNA^+ was detected among products. No reaction took place in the dark, or in the absence of $B(C_6H_5)_4^-$ as a counteranion, an alcohol as a solvent, or the Rh complex as a catalyst.[10] Meanwhile, (OEP)Zn^{II} in place of the Rh complex showed no catalytic activity at all. The formation of BNAH (λ_{max} 352 nm) was monitored by electronic spectroscopy, while (OEP)Rh^{III}-$COCH_3$ was found to undergo no spectral change during reaction. Irradiation of a solution containing the Rh complex and $NaB(C_6H_5)_4$ resulted in bleaching of the complex. $BAP^+B(C_6H_5)_4^-$[8] in C_6H_6-CH_3CN-CH_3OH (3:3:10 v/v) was photoreduced in a similar manner as observed for $BNA^+B(C_6H_5)_4^-$ and gave BAPH (Eq. 3). When this reaction was carried out in a solvent containing CH_3OD, a deuterium atom was incorporated into the 4-position of BAPH, as confirmed by the ^1H NMR analysis. These results suggest that the Rh-porphyrin catalyzes the generation of reactive hydride "H^-" upon photochemical oxidation of $B(C_6H_5)_4^-$ in an alcohol (as a proton source) ($ROH + B(C_6H_5)_4^- + h\nu \rightarrow (RO)B(C_6H_5)_2 + C_6H_5\text{-}C_6H_5 + \text{"}H^-\text{"}$) and its highly regioselective transfer to the 4-positions of pyridinium rings.

The photosensitized hydride transfer was found to be generally applicable to the reduction of "commom" electrophiles with a variety of hydride donors such as $NaBH_4$, alkoxides, and BNAH.[11] Thus, irradiation of a mixture of $NaBH_4$ (4.6 x 10^{-4} mol), dodecyl bromide (4.1 x 10^{-4} mol), and (OEP)Rh^{III}-$COCH_3$ (5.3 x 10^{-6} mol) in THF for 20 h gave dodecane (2150% based on the Rh complex) as the sole organic product.[12] When $NaBD_4$ was used, dodecane-d_1 (by mass spectrum) was formed with a kinetic isotope effect of $k(BH_4^-)/k(BD_4^-) \cong 2$ as regards its formation rate. These results confirm that the Rh complex catalyzes hydride transfer from BH_4^- to an alkyl bromide, ruling out the possibility of homolytic processes leading to alkyl radicals which abstract a hydrogen atom from the solvent. A similar photoreduction of dodecyl bromide took place with sodium ethoxide as a hydride donor in THF in the presence of an equivalent amount of 18-crown-6, giving rise to dodecane (in 1440% yield after 26 h)[12] and the equivalent amount of acetaldehyde which was identified as its 2,4-dinitrophenylhydrazone. The reduction of a ketone (cyclohexanone, 5.1 x 10^{-4} mol) with BNAH (8.4 x 10^{-4} mol) in CH_3OH-C_6H_6 (7:3 v/v) was also photosensitized with (OEP)Rh^{III}-$COCH_3$ (2.7 x 10^{-6} mol) and gave cyclohexanol (1850% after 46 h).[12]

The stoichiometric hydride transfer from $NaBH_4$, alkoxide, or BNAH to the Rh^{III} center of (OEP)Rh^{III}-Cl took place readily under photochemical conditions or even in the dark.[13] The present complex, (OEP)Rh^{III}-$COCH_3$, on the other hand, was stable toward these reagents in the dark, but underwent bleaching when irradiated in the absence of any hydride acceptors. These results, coupled with our previous finding on facile migration of a carbanion from Rh to the meso-position of organorhodium OEP derivatives (Eq. 4, in a schematic form),[15] suggest a catalytic mechanism for the present reactions as shown in Scheme 1; photochemical hydride transfer from a donor (X-H; $B(C_6H_5)_4^-$ + alcohol, BH_4^-, alkoxide, or BNAH) to $(OEP)Rh^{III}-COCH_3$ to give the reduced intermediate (**1** $\rightleftharpoons$ **2**), which subsequently transfers its hydride rapidly to an electrophile (Y; BNA^+, BAP^+, RBr, or ketone) or, in its absence, undergoes protonation leading to bleaching of the catalyst.



$$\overset{R}{—Rh—} \xrightarrow{RLi} \left[\begin{array}{c}R\\ —Rh—\\ R\end{array}\right]^- \longrightarrow \left[\,—\overset{R}{Rh}—C\begin{array}{l}R\\ H\end{array}\right]^- \xrightarrow{[O]} —\overset{R}{Rh}—R \qquad (4)$$



Scheme 1.

This work has been based on our previous finding that $(OEP)Rh^{III}-Cl$ is an excellent hydride carrier.[14] That the Rh^{III} ion tends to undergo 2e redox reactions seems to be rather general.[6a-d] The present study shows that the redox reactivity of a Rh porphyrin is controlled by the introduction of an acetyl ligand to the axial site of Rh, so that it can be used as a hydride mediator under photochemical conditions. This finding will enlarge the scope and potentiality of photo-induced redox reactions in general, since the hydride ion (H^-), metal-bound[16] or fixed in NAD(P)H models,[17] can undergo ready reactions, usually without catalyst, with a variety of electrophiles including H^+, C=O, C=N, and activated C=C double bonds.

This work was supported by a Grant-in-Aid for Scientific Research (No. 61540441) from the Ministry of Education, Science, and Culture.

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8) Prepared by the reaction of $NaB(C_6H_5)_4$ with BNA^+Cl^- or BAP^+Cl^- in acetone.

9) The reaction mixture was chromatographed on silica gel with $CHCl_3$ as an eluant to give $(OEP)Rh^{III}-COCH_3$ (identified by ^1H NMR and electronic spectra) and BNAH (identified by comparison of its ^1H NMR, fluorescence, and electronic spectra with those of the authentic sample).

10) $(OEP)Rh^{III}-Cl$ was able to catalyze a similar photoreduction of $BNA^+B(C_6H_5)_4^-$, but the identity of the axial ligand in the catalytically active species was not clear. When $(OEP)Rh^{III}-CH_3$ was used, it underwent facile photochemical Rh-C bond cleavage, and then catalyzed the reduction of the BNA^+ salt.

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13) For the reaction $(OEP)Rh^{III}-Cl + BH_4^- \longrightarrow (OEP)Rh-H + \text{"}BH_3\text{"}$, see Ref. 14. $(OEP)Rh^{III}-Cl$ also reacts with RO^- ($R = CH_3$, CH_3CH_2, and $(CH_3)_2CH$) in ROH to give $[(OEP)Rh^I]^-$ and a carbonyl compound identified as its 2,4-dinitriphenylhydrazone. This reaction is thermally accessible but is photo-accelerated. A quite facile hydride transfer takes place between $(OEP)Rh^{III}-Cl$ and BNAH in an inert solvent to give (OEP)Rh-H and BNA^+Cl^-. This reaction is not detected for an alcohol solution, but reduction of the rhodium complex takes place when the solution is irradiated.

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(Received May 30, 1987)