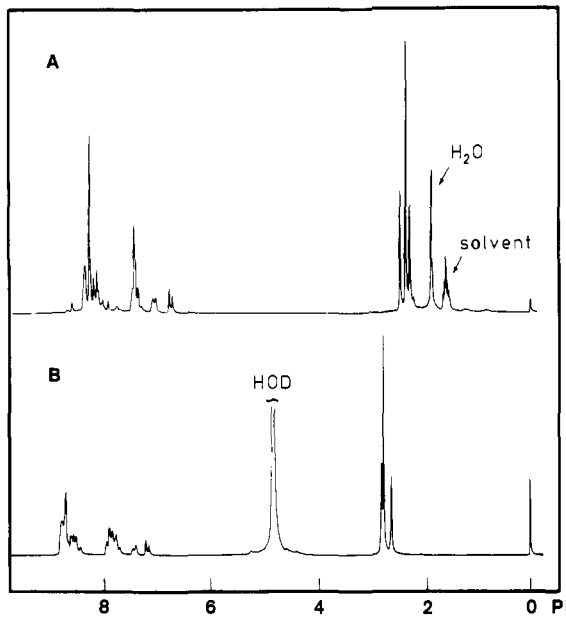

Figure 2. 100-MHz ^1H NMR spectra of $[Ru(tpy)(bpic)(C_3H_6N)]^{3+}$ in CD_3CN (A) and 0.1 M DCl (B) (Me_4Si external standard).

a reversible couple $E_{1/2}$ = 1.09 V for the amine precursor), with a peak on the reverse sweep ($E_{p,c}$ = 0.68 V) associated with the four-electron oxidation product, as shown in Figure 1. The ^1H NMR spectrum (in CD_3CN) showed two doublets in the aliphatic region centered at 1.12 and 1.62 ppm with very small coupling (0.73 and 1.56 Hz, respectively). This spectrum is consistent with the imine formulation, with both methyl groups being split by the adjacent NH=C moiety. On addition of a drop of D_2O, each doublet collapses to a singlet consistent with deuterium exchange at the imine NH group. We conclude therefore that the two-electron oxidation product is the isopropylimine complex $[Ru(tpy)(bpy)(NH{=}CMe_2)]^{2+}$ and that the small blue shift in the visible spectrum on going from the amine to imine ligand indicates there is a relatively small amount of back-bonding from Ru(II) to the isolated monodentate imine, compared with the large effect observed for the conjugated α,α'-diimine grouping.[1]

The four-electron oxidation product has the general formula $[Ru(tpy)(bpy)(C_3H_6N)]_z(PF_6)_{3z}$ by microanalysis,[5] and conductance measurements in acetonitrile using Feltham's method[6] show that the molecular complexity z = 1, so the complex is monomeric. ^1H NMR spectra of the related complex $[Ru(tpy)(bpic)(C_3H_6N)]^{3+}$ (bpic = 4,4'-dimethyl-2,2'-bipyridine) in acetonitrile-d_3 and 0.1 M DCl are shown in Figure 2. In the aliphatic region, each spectrum contains a six-proton methyl singlet due to the oxidized isopropylamine ligand, flanked by two three-proton methyl singlets arising from the dimethylbipyridine ligand. The complex shows little absorption in the visible region of the electronic spectrum, consistent with oxidation of the metal center to Ru(III)[7] or Ru(IV).[8] In dry acetonitrile solution, cyclic voltammetry shows a reversible couple, $E_{1/2}$ = 0.72 V (Figure 1).

The above evidence indicates the $NCMe_2$ skeleton remains intact in the four-electron oxidation product, which can be regarded formally as a Ru(IV) complex of the coordinated isopropylideneamide anion, $(N{=}CMe_2)^-$. Such a ligand has several possible bonding modes,[9] but the ready electrochemical interconversion of this complex with the imine species leads us to believe that it functions as an N-bound mononuclear ligand in this case. Application of the 18-electron rule for the metal center suggests the ligand should be a four-electron donor, implying Ru-N multiple bonding and a linear Ru-N-C linkage. The ^1H NMR studies are in agreement with this structure, and we are undertaking an X-ray structural analysis to confirm the assignment.

The electrochemical interconversion of the two- and four-electron oxidation products of coordinated isopropylamine occurs since on oxidation of the isopropylimine species (presumably at the metal center), the acidity of the proton on the ligating imine nitrogen would be markedly increased[10] and deprotonation gives rise to the coordinated isopropylideneamide anion. It is apparent from the cyclic voltammetric behavior of the isopropylimine and isopropylideneamide complexes (Figure 1B,C) that the oxidation of the former to the latter is more rapid than the reverse process. The cathodic shift in potential for the $E_{p,a}$ of the complex of the isopropylideneamide anion relative to the isopropylimine species reflects the unusual nature of the Ru-ligand interaction in the former complex. The concept of assignment of a formal oxidation state to the metal center is clearly inappropriate for this species, and this is further evidenced by its magnetic properties, which reveal a slight paramagnetism (μ_{eff} = 1.2 μ_B).

Details of the characterization, and chemical and electrochemical behavior of the imine and isopropylideneamide anion complexes of $Ru(tpy)(bpy)^{n+}$, will be published subsequently.

Acknowledgment. We thank Dr. T. G. Appleton (University of Queensland) for recording the 100-MHz ^1H NMR spectra. This research was supported by the Australian Research Grants Committee.

(5) Anal. Calcd. for $[Ru(tpy)(bpy)(C_3H_6N)]_z(PF_6)_{3z}$: C, 34.3; H, 2.6; N, 8.6; P, 9.4; F, 34.8. Found: C, 34.0, H, 2.7; N, 8.4; P, 9.1; F, 34.8.

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Ru(bpy)$_3^{2+}$-Mediated Photoreduction of Olefins with 1-Benzyl-1,4-dihydronicotinamide: A Mechanistic Probe for Electron-Transfer Reactions of NAD(P)H-Model Compounds[1]

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Nonenzymatic reductions of various substrates with 1,4-dihydropyridines are of interest as models for biological oxidation-reduction reactions involving the pyridine nucleotide coenzymes.[2] The reduction of carbon-carbon double bond is limited to the reactions of electron-deficient olefins with Hantzsch compounds at elevated temperatures[3] and to the reduction of very electron-poor olefins by 1-alkyl-1,4-dihydronicotinamides.[4] Although the mechanism still remains uncertain, it was demonstrated that direct hydrogen transfer from the reductants to olefins is involved.[3b,4,5] In this communication we wish to report that

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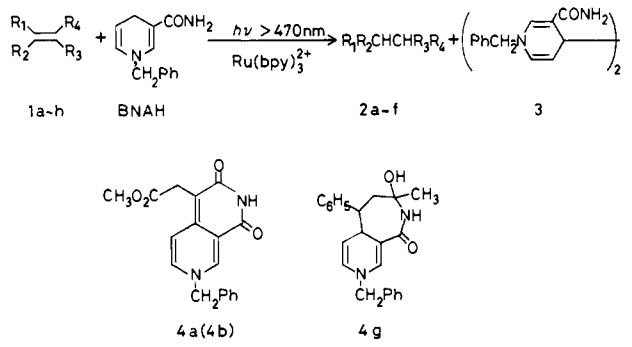
Table I. $Ru(bpy)_3^{2+}$-Mediated Photoreduction of Olefins with 1-Benzyl-1,4-dihydronicotinamide[a]

	olefin (1)						yield,[d] %		
	R_1	R_2	R_3	R_4	$-E_{p/2}^{red}$,[b] V	solvent[c]	2[e]	3[f]	4[g]
a	CO_2CH_3	H	H	CO_2CH_3	2.16	10:1 py-MeOH	96	35	0
						DMF	90		
						MeCN	47	18	
						MeOH	36	19	14
b	CO_2CH_3	H	CO_2CH_3	H	2.00	10:1 py-MeOH	68	34	tr
						DMF	20		
						MeCN	31		
						MeOH	9	21	29
c	p-CNC_6H_4	H	CN	H	1.97	10:1 py-MeOH	61	16	
						MeOH	22	tr	
d	p-CNC_6H_4	H	H	CN	1.98	10:1 py-MeOH	67	24	
						MeOH	27	tr	
e	p-$CH_3OCOC_6H_4$	H	CN	H	2.02	10:1 py-MeOH	33	13	
f	C_6H_5	CN	C_6H_5	H	2.07	10:1 py-MeOH	33		
g	C_6H_5	H	$COCH_3$	H	2.20	10:1 py-MeOH	0	0	37
						MeOH	0	0	38
h	C_6H_5	H	CN	H	2.37	10:1 py-MeOH	0[h]	0[h]	0[h]

[a] For solutions containing BNAH (0.1 M), **1** (0.05 M), and $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (1 mM). [b] Determined by cyclic voltammetry vs. Ag/Ag^+ in acetonitrile. [c] py = pyridine, MeOH = methanol, DMF = *N,N*-dimethylformamide, and MeCN = acetonitrile. [d] At 100% conversion of olefins. [e] GLC or NMR yields based on 1 used. [f] Isolated yields based on BNAH used. [g] Isolated yields based on 1 used. [h] No consumption of the olefin was observed.

Scheme I



several olefins which are unreactive with 1,4-dihydropyridines in the dark at room temperature[3-5] can be reduced by 1-benzyl-1,4-dihydronicotinamide (BNAH) upon selective photoexcitation of $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) and that the photomediated two-electron reduction proceeds by way of sequential electron transfer.

Irradiation of a solution containing $Ru(bpy)_3Cl_2 \cdot 6H_2O$, an olefin (**1a-h**), and BNAH at >470 nm[6] gave **2a-f**, **3**, and/or **4** but did not result in the consumption of **1h** (Scheme I and Table I). The structures of **4a**[7] and **4g**[8] were determined from their spectroscopic properties and elemental composition data.[9] It was found that magnesium ion exerts a profound effect on the photomediated reduction of **1b** in methanol (Figure 1) as observed in the ground-state reduction of olefins.[4,5]

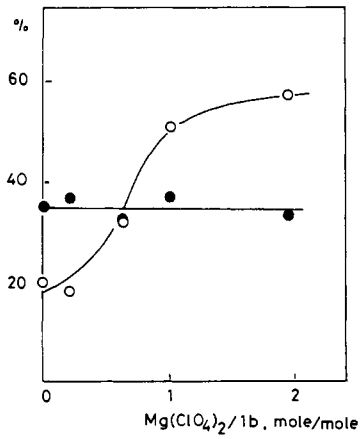


Figure 1. Yields of **2b** (○) and conversions of **1b** (●) vs. $[Mg(ClO_4)_2]$; methanol solutions; >470-nm irradiation; [**1b**] = 0.1 M, [BNAH] = 0.05 M, $[Ru(bpy)_3^{2+}] = 1 \times 10^{-3}$ M.

Table II. Deuterium Isotopic Distribution in the Reduction Product from $Ru(bpy)_3^{2+}$-Mediated and Direct Photoreactions of Dimethyl Maleate and Fumarate

			yield,[a] %		
	olefin	deuteration reagent	2a-d_0	2a-d_1	2a-d_2
$Ru(bpy)_3^{2+}$-mediated photoreduction[b]	1a	BNAH-4,4-d_2[c]	99	1	0
		CH_3OD	4	37	59
		CD_3OD	4	37	59
		CH_3OD[d]	0	22	78
	1b	BNAH-4,4-d_2	94	6	0
		CH_3OD	3	38	59
direct photoreduction[e]	1a	BNAH-4,4-d_2	53	47	0
	1b	BNAH-4,4-d_2	38	62	0

[a] Determined by GC-mass analyses. [b] Unless otherwise specified, the photoreactions were carried out in 10:1 pyridine-methanol (or deuterated methanol) by using $Ru(bpy)_3Cl_2 \cdot 6H_2O$. [c] The isotopic purity was over 98%. [d] The ruthenium complex and BNAH were used after single recrystallization from D_2O and CH_3OD, respectively. [e] Performed by the direct photoexcitation of BNAH-4,4-d_2 at >360 nm in the absence of the ruthenium complex.

In order to obtain insights into the mechanism, deuteration experiments were performed by using BNAH-4,4-d_2, metha-

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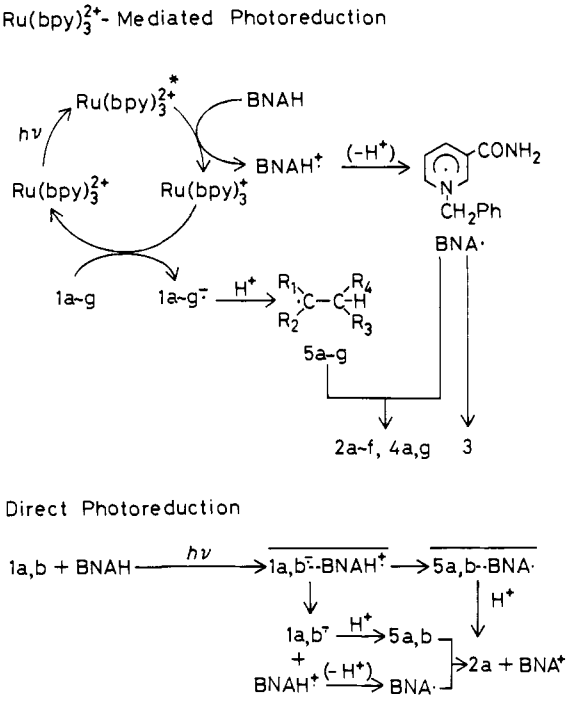
(6) A filter solution (1-cm path length) containing potassium chromate (30 g/L), sodium nitrate (300 g/L), and sodium hydroxide (10 g/L) was used. The progress of the reactions was followed by GLC, HPLC, and NMR spectroscopy, especially for the reduction of **1a** and **1b**.

(7) Mp 232–235 °C dec; UV λ_{max} (CH_3OH) 363 nm (ϵ 23 000); ^1H NMR (Me_2SO-d_6) δ 3.43 (s, 2 H), 3.59 (s, 3 H), 5.21 (s, 2 H), 6.77 (d, J = 7.4 Hz, 1 H), 7.37 (br s, 5 H), 7.50 (dd, J = 1.6 and 7.4 Hz, 1 H), 8.47 (dd, J = 1.6 and 2 Hz, 1 H), 10.72 (br s, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 29.12, 51.15, 58.36, 95.45, 110.68, 113.01, 127.03–128.61 (4 C), 135.70, 135.88, 140.45, 141.62, 162.36, 164.12, 171.50; mass spectrum, m/e 324 (M^+). Anal. Calcd for $C_{18}H_{16}N_2O_4$: C, 66.66; H, 4.97; N, 8.64. Found: C, 66.53; H, 4.90; N, 8.74.

(8) Mp 206–207 °C dec; UV λ_{max} (CH_3OH) 345 nm (ϵ 5020); ^1H NMR ($CDCl_3$) 2.20 (s, 3 H), 2.66 (dd, J = 2 and 18 Hz, 1 H), 3.20 (dd, J = 10 and 18 Hz, 1 H), 3.40 (dd, J = 2 and 10 Hz, 1 H), 3.68 (dd, J = 2 and 5 Hz, 1 H), 4.00 (s, 2 H), 4.66 (dd, J = 5 and 8 Hz, 1 H), 5.64 (dd, J = 2 and 8 Hz, 1 H), 6.24 (br s, 1 H), 6.60 (m, 2 H), 7.35 (br s, 5 H); mass spectrum m/e 360 (M^+). Anal. Calcd for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.91; H, 6.70; N, 7.84.

(9) Attempts for isolation of similar adducts with the other olefins were not made.

Scheme II



nol-*O*-*d*, or methanol-d_4 in the photomediated reduction of **1a** and **1b**. The results shown in Table II demonstrate that hydroxylic protons of methanol are predominantly involved in the reduction pathway,[10] i.e., direct hydrogen transfer from BNAH to the olefins is negligible. In these reactions there was observed neither stereomutation of **1a** and **1b** nor deuterium incorporation in the recovered olefins even at 50–80% conversions. Moreover, an identical deuterium isotopic distribution in the reduced product was obtained with either methanol-d_4 or methanol-*O*-*d*. These observations unambiguously eliminate the possibilities that the half-reduced species of the olefins would disproportionate or abstract a hydrogen atom from methanol or BNAH to give the reduced product. Therefore we conclude that the photomediated reduction of **1a** and **1b** occurs as a consequence of sequential two-electron transfer from BNAH to the olefins; a similar mechanism should operate in the reduction of the other olefins.

It was found that the luminescence of Ru(bpy)$_3^{2+}$ was efficiently quenched by BNAH but not by the olefins except **1f**.[11] The quenching rate constant in acetonitrile (3.5×10^8 M^{-1} s^{-1}) approximately falls on a value predicted for electron-transfer quenching of excited Ru(bpy)$_3^{2+}$ by electron donors,[12] demonstrating that one-electron transfer from BNAH to the excited ruthenium complex is responsible for the initiation process. Therefore, the first one-electron reduction appears to occur by electron transfer from Ru(bpy)$_3^+$ to the olefins that have a reduction potential of ≥ -2.2 V where an energy demand for the process might be met.[13] In protic media the anion radical of **1** (**1**$^-$·) so formed should be rapidly protonated to give the neutral radicals (**5a–g**) that are probably susceptible to the second one-electron reduction.

It is known that BNAH$^+$· is readily deprotonated by a base to yield BNA· which has a relatively low oxidation potential.[14] In the second one-electron reduction, therefore, BNA· probably donates an electron to **5**, a mechanism supported by the fact that yields of both **2** and **3** increase with an increase in the basicity of solvent; an increase of the basicity of solvent leads to higher steady-state concentrations of BNA·, thus enabling both one-electron reduction of **5** and dimerization of BNA· to have more chances.[15] In other words, the net two-electron reduction requires that the half-reduced species (**5**) be high enough in their reduction potentials to receive an electron from BNA·; **5a–f** might fit the case since an electron-withdrawing group is located at the radical center. On the other hand, **5g** which has no extra electron-withdrawing group is perhaps incapable of being reduced by BNA·, thus undergoing a radical-coupling reaction to give **4g**. Scheme II delineates the reaction pathways of the photomediated reactions.

The present results can provide a speculation that the ground-state reduction of olefins by BNAH and probably by other NAD(P)H-model compounds may proceed via a sequential electron–proton–electron-transfer (ECE) mechanism.[16] If the ECE process occurs in a solvent cage, direct hydrogen transfer should be involved as observed.[3b,4,5] In this regard, it should be noted that the direct photoreduction of **1a** and **1b**[17] with BNAH-4,4-d_2 at >360 nm (in the absence of Ru(bpy)$_3^{2+}$) gave both **2a**-d_0 and -d_1 in comparable amounts (Table II), indicating the partial involvement of direct hydrogen transfer in the reduction pathway. Since the quenching of BNAH fluorescence by electron acceptors involving **1a** and **1b** has been reported to occur by means of an electron-transfer mechanism,[18] the ion-radical pair (BNAH$^+$·–**1**$^-$·) which should be initially formed might undergo proton transfer from BNAH$^+$· to **1**$^-$· in a solvent cage, competitively with its dissociation into free ion radicals.

Preliminary experiments showed that the ground-state reduction of olefins by BNAH is limited to such olefins which have a reduction potential from >–1.6 to –1.7 V, the possible limit for the occurrence of the first one-electron transfer. The Ru(bpy)$_3^{2+}$ photomediation activates the first one-electron reduction, thus extending the lower limit of reduction potential of olefins to ~–2.2 V. On the other hand, magnesium ion would activate the second one-electron reduction as well though the origin of its effects is not known. Further investigations are in progress.

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(10) In the deuteration experiments with methanol-*O*-*d* and -d_4, Ru(bpy)$_3$Cl$_2$·6H$_2$O and BNAH both of which have exchangeable protons were used without thorough H–D exchange for convenience, thus giving significant amounts of **2a**-d_0 and -d_1. In fact, the formation of **2a**-d_2 was remarkably improved when the ruthenium complex and BNAH obtained by single recrystallization from deuterium oxide and methanol-*O*-*d*, respectively, were used.

(11) The Stern–Volmer constants ($k_q\tau$) for the phosphorescence quenching by BNAH under deaerated conditions are 358 (10:1 pyridine–methanol), 294 (acetonitrile), 184 (DMF), and 120 M^{-1} (methanol), while the values for the quenching by the olefins are less than 5 M^{-1} in any solvent with one exception (210 M^{-1} for **1f** in acetonitrile).

(12) (a) The calculated rate constant is 7.5×10^8 M^{-1} s^{-1}, on the basis of the Rehm–Weller's equation used for the quenching of the Ru(bpy)$_3^{2+}$ phosphorescence by electron donors.[12b] A published oxidation potential (0.76 V vs. SCE in acetonitrile)[18] was used for the calculation. (b) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1978**, *100*, 7219.

(13) The redox potential of the Ru(bpy)$_3^{2+/+}$ couple was determined by cyclic voltammetry to be –1.85 V vs. Ag/Ag$^+$ in aceonitrile, whereas the reduction potentials of the olefins listed in Table I were obtained as half-peak potentials from irreversible cyclic voltamograms. Therefore, free-energy changes associated with the one-electron transfer process cannot be exactly estimated. However, it is notable to point out that the redox potential of the Ru(bpy)$_3^{2+/+}$ couple is close to the reduction potential of **1g** (–2.20 V), perhaps the lowest limit for the occurrence of electron transfer from Ru(bpy)$_3^+$ to olefins at room temperature.

(14) (a) Blaedel, W. J.; Haas, R. G. *Anal. Chem.* **1970**, *42*, 918. (b) The cathodic half-peak potential of BNA$^+$ was determined to be –1.33 V vs. Ag/Ag$^+$ in acetonitrile. See also: Cunningham, A. J.; Underwood, A. L. *Biochemistry* **1967**, *6*, 266.

(15) A referee pointed out that reduction would also involve

$$\text{BNAH}^+\cdot + \text{Ru(bpy)}_3^{2+} \rightarrow \text{BNA}^+ + \text{Ru(bpy)}_3^+ + \text{H}^+$$

with Ru(bpy)$_3^+$ serving as the second donor. This and other possibilities should be considered in establishing the detailed mechanism.

(16) Gase and Pandit suggested that the electron–proton–electron-transfer mechanism is unfavorable for the magnesium-catalyzed reduction of 2-cinnamoylpyridine, since a deuterium atom of BNAH-4,4-d_2 was transferred to the β position to the carbonyl group of the substrate.[5] A hydride-transfer or electron–hydrogen-atom-transfer mechanism was employed for choice.

(17) Ohnishi, Y.; Kagami, M. *Chem. Lett.* **1975**, 125.

(18) Martens, F. M.; Verhoeven, J. W.; Gase, R. A.; Pandit, U. K.; Boer, T. J. D. *Tetrahedron.* **1978**, *34*, 443.