Mechanisms of Reductive Methylation of NAD^+ Analogues by a *trans*-Dimethylcobalt(III) Complex

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Various NAD^+ analogues are readily reduced by a *trans*-dimethylcobalt(III) complex, *trans*-[$CoMe_2$(L)] (L = 11-hydroxy-2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1-olate), to yield the corresponding methylated NADH analogues, while *cis*-dialkyl- or monoalkylcobalt(III) complexes show no reactivity towards NAD^+ analogues. The charge distribution of the NAD^+ analogues, as well as the thermodynamic stability of the products, is shown to be an important factor in determining the isomer distribution of the methylated products. The observed second-order rate constants for the reduction of NAD^+ analogues by *trans*-[$CoMe_2$(L)] in acetonitrile at 298 K are much larger than those estimated for outer-sphere electron transfer from *trans*-[$CoMe_2$(L)] to NAD^+ analogues.

There has been considerable interest in the reduction of pyridinium ions used as nicotinamide adenine dinucleotide (NAD^+) analogues to the corresponding dihydropyridines.[1-3] Reduction of pyridinium ions by organometallic reagents to yield substituted dihydropyridines has also been extensively studied, since the substituted dihydropyridines are valuable synthetic intermediates for a variety of alkaloids as well as NADH analogues.[4] With respect to the alkylating reagents, however, they have so far been limited to strong reductants, such as alkyllithium,[4] alkyl-Grignard,[4,5] alkylzinc,[6] and alkylcopper[7] reagents.

On the other hand, the vitamin B_{12} coenzyme and related alkylcobalamins are well known as unique, naturally occurring organometallic reagents of great biological significance.[8] However, there has so far been no report on the reduction of NAD^+ analogues by alkylcobalt(III) complexes which are known to be rather mild reducing reagents.[9] In this study,[10] we report that various NAD^+ analogues can be readily reduced by a *trans*-dialkylcobalt(III) complex, *trans*-[$CoMe_2$(L)](L = 11-hydroxy-2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1-olate) to yield the corresponding methylated NADH analogues. Mechanisms of the reductive methylation of NAD^+ analogues by *trans*-[$CoMe_2$(L)] complex are discussed, based on the isomer distribution of the methylated products as well as the dependence of the observed second-order rate constants on the one-electron reduction potentials of NAD^+ analogues.

Experimental

Materials.—The preparation of (1-X-benzyl)nicotinamidinium perchlorates (X-$BNA^+ClO_4^-$: X = H, 4-NO_2, 4-MeO and 2,4-Cl_2) and 10-methylacridinium perchlorate ($AcrH^+ClO_4^-$) have been described previously.[11,12] 1-Methyl-X-quinolinium iodides [X-QuH(I): X = H, 2-Me, 3-CN and 3-Br] were prepared by reaction of the corresponding quinolines with methyl iodide in acetone.[13] The quinolinium cations were obtained as the perchlorate salts by the addition of magnesium perchlorate to the iodide salts in water, and purified by recrystallization from hot methanol. Alkylcobalt(III) complexes, *trans*-[$CoMe_2$(L)] (L = 11-hydroxy-2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1-olate),[14,15] *cis*-[CoR_2(bipy)$_2$]ClO_4 (R = Me, Et, or $PhCH_2$; bipy = 2,2′-bipyridine),[15,16] and [CoR(Hdmg)$_2$(py)] (R = Me or Et; Hdmg = dimethylglyoximato; py = pyridine)[15,17] were prepared as described previously. Acetonitrile, which was also obtained commercially, was purified and dried with calcium hydride by the standard procedure and stored under nitrogen.

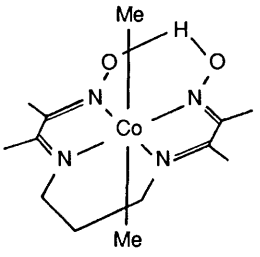
Reaction Procedure.—After a [$^2H_3$]acetonitrile (CD_3CN) solution (0.60 cm^3) containing $BNA^+ClO_4^-$ (4.0×10^{-2} mol dm^{-3}) and *trans*-[$CoMe_2$(L)] (4.1×10^{-2} mol dm^{-3}) in an NMR tube had been deaerated by bubbling with argon gas, it were allowed to stand for 2 h at room temperature. The products were identified by elementary analysis as well as by comparison with the ^1H NMR spectra in the literature.[13] The ^1H NMR spectroscopy measurements were carried out using a Japan Electron-Optics JNM-PS-100 ^1H NMR or JEOL JNM-GSX-400 ^1H NMR spectrometer. The isomers can be readily distinguished by the methyl and/or methylene resonances of the ^1H NMR spectra: δ_H(CD_3CN, 400 MHz) AcrH(Me): $\delta(CH_3)$ 3.35 and 1.24; 1,2-QuH(Me): $\delta(CH_3)$ 2.84 and 1.04; 3-CN-1,2-QuH(Me): $\delta(CH_3)$ 2.90 and 1.19; 3-CN-1,4-QuH(Me): $\delta(CH_3)$ 3.22 and 1.33; 3-Br-1,2-QuH(Me): $\delta(CH_3)$ 2.88 and 1.15; 3-Br-1,4-QuH(Me): $\delta(CH_3)$ 3.27 and 1.31; 2-Me-1,2-QuH(Me): $\delta(CH_3)$ 2.85 and 1.33; 1,6-BNA(Me): $\delta(CH_2)$ 4.47, $\delta(CH_3)$ 0.97; 1,4-BNA(Me): $\delta(CH_2)$ 4.37, $\delta(CH_3)$ 1.11; and 1,2-BNA(Me): $\delta(CH_2)$ 4.42, $\delta(CH_3)$ 1.01.

Cyclic Voltammetry.—The cyclic voltammetry measurements were performed on a Hokuto Denko Model HA-301 potentiostat–galvanostat at 298 K in MeCN containing 0.10 mol dm^{-3} $NBu^n_4ClO_4$ as supporting electrolyte by using a saturated calomel electrode (SCE) as reference under deaerated conditions. The one-electron reduction potentials of NAD^+ analogues were determined by analysing the cyclic voltammograms at various sweep rates in the range 10–1500 mV s^{-1}, based on the method previously reported.[1,11] The platinum microelectrode was routinely cleaned by soaking it in concentrated nitric acid, followed by repeated rinsing with water and acetone, and drying at 353 K prior to use.

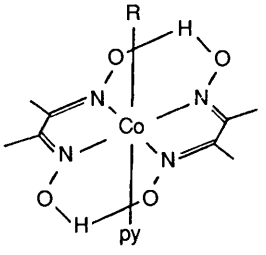
Kinetic Measurements.—Rates of the reduction of NAD^+ analogues by *trans*-[$CoMe_2$(L)] were monitored by measuring the disappearance of the absorbance due to *trans*-[$CoMe_2$(L)] (λ_{max} = 407 nm, $\varepsilon = 6.0 \times 10^3$ dm^3 mol^{-1} cm^{-1}) using a Union SM-401 spectrophotometer. Kinetic measurements were carried out under pseudo-first-order conditions where the concentrations of NAD^+ analogues were maintained at greater than ten times the excess of the concentration of *trans*-[$CoMe_2$(L)]. All the rate constants were determined by a least-squares curve fit by using a microcomputer.

Results and Discussion

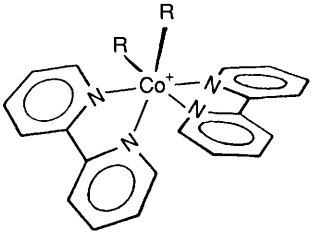
Product Distribution.—The alkylcobalt(III) complexes used in this study are shown in Fig. 1. Alkylcobaloximes, [CoR(Hdmg)$_2$-



trans-[$CoMe_2(L)$]



[$CoR(Hdmg)_2(py)$]



cis-[$CoR_2(bipy)_2$]$^+$

Fig. 1 Alkylcobalt(III) complexes

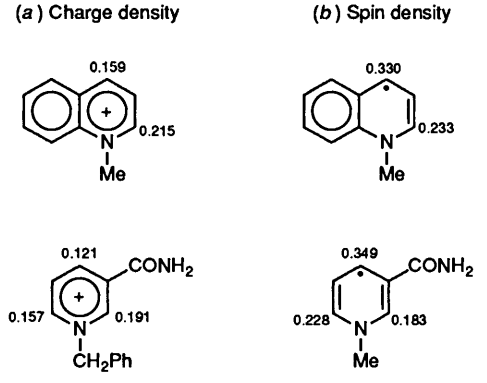


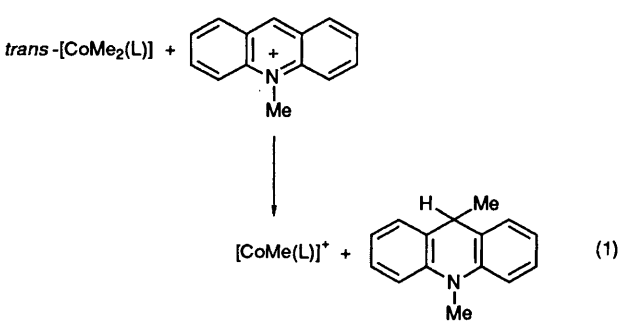
Fig. 2 (*a*) Charge densities of QuH^+ and BNA^+. (*b*) Spin densities of $QuH^{\bullet}$p and $BNA^{\bullet}$. The calculations were performed using the MNDO method.[21]

(py)] (R = Me and Et), frequently used as coenzyme B_{12} analogues,[18] showed no reactivity towards 10-methylacridinium ion ($AcrH^+$) which is known to be a relatively strong oxidant among various NAD^+ analogues.[11] Dialkylcobalt(III) complexes, *cis*-[$CoR_2(bipy)_2$]ClO_4 (R = Me, Et and $PhCH_2$), which are stronger reductants than [$CoR(Hdmg)_2(py)$],[19] also did not react with $AcrH^+$ in acetonitrile. When a sterically less-hindered dialkylcobalt(III) complex, as compared with the *cis*-dialkylcobalt(III) complexes, *trans*-[$CoMe_2(L)$] (Fig. 1), is used as a reductant, however, $AcrH^+$ is readily reduced by *trans*-[$CoMe_2(L)$] to yield 9,10-dimethylacridine [AcrH(Me)] selectively [reaction (1)]. The formation of $[CoMe(L)]^+$ was confirmed by ^1H NMR spectroscopy.[19] The *trans*-[$CoMe_2(L)$] complex can also reduce other NAD^+ analogues, 1-methylquinolinium ions (X-QuH^+; X = 3-CN, 3-Br, H and 2-Me) and 1-(X-benzyl)nicotinamidium ion (X-BNA^+; X = 4-NO_2, 2,4-Cl_2, 4-Cl, H and 4-MeO) to yield the corresponding methylated NADH analogues (methylated 1,2- and 1,4-dihydroquinolines, as well as 1,6-, 1,4-, and 1,2-dihydronicotinamides). The relative amounts of the isomers present in the initial product mixtures were determined from the ^1H NMR (400 MHz) spectra under conditions such that the amount of a reductant was slightly in excess of that of the NAD^+ analogue in order to avoid the possible isomerization in the presence of the unchanged NAD^+ analogue, as reported in the literature.[20] The product distributions are shown in Table 1. For the reduction of X-QuH^+, the 1,2-isomers predominate and no or only a little of the 1,4-isomer is formed. In the case of BNA^+, the 1,6-isomer predominates, but a comparable amount of the 1,4-isomer is formed together with a small amount of the 1,2-isomer.

Origin of the Isomer Distribution.—The MO calculation using the MNDO method (modified neglect of diatomic orbitals)[21] reveals that the charge density of QuH^+ is greatest at the C-2 position (0.215) as compared with that at the C-4 position (0.159) as shown in Fig. 2(*a*). In contrast, the spin density of $QuH^{\bullet}$ is greatest at the C-4 position (0.330) as compared with that at the C-2 position (0.233), as shown in Fig. 2(*b*). Thus, the charge distribution of QuH^+ rather than the spin distribution of $QuH^{\bullet}$ may be an important factor in determining the isomer distribution in Table 1, suggesting that the reduction of QuH^+ may proceed *via* transfer of methyl anion from *trans*-[$CoMe_2(L)$] to QuH^+. The charge densities of BNA^+ at the C-2, C-4 and C-6 positions are also calculated as 0.191, 0.121 and 0.157, while the spin densities of $BNA^{\bullet}$ at the C-2, C-4 and C-6 positions are obtained as 0.183, 0.349 and 0.288, respectively (Fig. 2). The ΔH_f (heat of formation) values of the 1,2-, 1,4- and 1,6-isomers are calculated by using the MNDO method with the geometrical parameters optimized.[21] The ΔH_f values are listed in Table 2, where the ΔH_f value of the 1,2-isomer (−37 kJ mol^{-1}) is 9–10 kJ mol^{-1} larger than that of the 1,6-isomer (−47 kJ mol^{-1}) and the 1,4-isomer (−46 kJ mol^{-1}). Thus, the reason for the small isomer distribution at the C-2 position, in spite of the greater charge density, may be ascribed to the instability of the 1,2-isomer as compared to the 1,6- and 1,4-isomers. In consequence, the charge distribution of NAD^+ analogues together with the thermodynamic stability of the products may determine the isomer distribution.

Kinetics and Mechanism.—The rates of reduction of various NAD^+ model compounds by *trans*-[$CoMe_2(L)$] were followed by the decay of the absorption band due to *trans*-[$CoMe_2(L)$] (λ_{max}407 nm). The rates obeyed second-order kinetics, showing the first-order dependence on the concentration of each reactant. The observed second-order rate constants k_{obs} of various NAD^+ analogues are listed in Table 3. The k_{obs} values span a range of 10^5 from the smallest value of 3.5×10^{-4} for 2-MeQuH^+ to the largest value of 7.3×10 of 3-CNQuH^+.

We have previously determined the one-electron reduction potentials (E^0_{red}) of BNA^+ and derivatives as well as $AcrH^+$ by analysing the cyclic voltammograms at various sweep rates.[11] The E^0_{red} values of other NAD^+ analogues (QuH^+ and derivatives) can also be determined by analysing the cyclic voltammograms as follows. The cyclic voltammograms of QuH^+ and derivatives show well-defined cathodic waves but no



(1)

Table 1 Reduction of NAD^+ analogues (4.0×10^{-2} mol dm^{-3}) by *trans*-[$CoMe_2(L)$] (4.1×10^{-2} mol dm^{-3}) in acetonitrile at 298 K

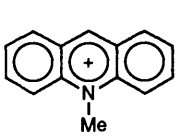
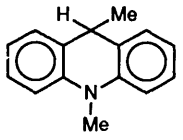
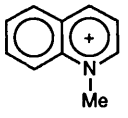
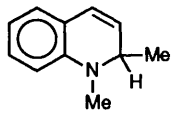
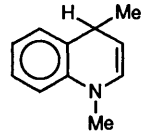
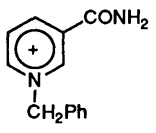
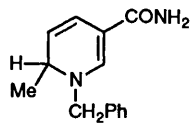
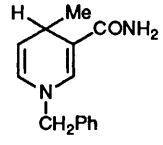
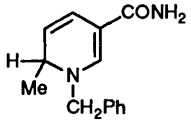
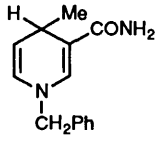
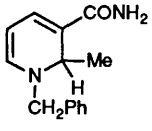
NAD^+ analogue	Product yield (%)		
 $AcrH^+$	 AcrH(Me) (100)		
 QuH^+ 3-$CNQuH^+$ 3-$BrQuH^+$ 2-$MeQuH^+$	 1,2-QuH(Me) (100) 3-CN-1,2-QuH(Me) (78) 3-Br-1,2-QuH(Me) (91) 2-Me-1,2-QuH(Me) (100)	 1,4-QuH(Me) (trace) 3-CN-1,4-QuH(Me) (22) 3-Br-1,4-QuH(Me) (9) 2-Me-1,4-QuH(Me) (trace)	
 BNA^+	 1,6-BNA(Me) (51)	 1,4-BNA(Me) (37)	 1,2-BNA(Me) (12)

Table 2 The ΔH_f (heat of formation) values of the methylated isomers

Isomer		$\Delta H_f{}^a$/kJ mol^{-1}
	1,6-BNA(Me)	−47
	1,4-BNA(Me)	−46
	1,2-BNA(Me)	−37

[a] Calculated by using the MNDO method with the geometrical parameters optimized.[21]

corresponding anodic waves on the reverse scan, as shown in Fig. 3. The transfer coefficient β defined by the tangent of the Gibbs energy change of electron transfer at the cathodic peak potential is obtained from the width of the wave $E^p_{red} - E^{p/2}_{red}$ by using eqn. (1).[11,12] On the other hand, the transfer

$$\beta = 1.857RT/[F(E^p_{red} - E^{p/2}_{red})] \quad (1)$$

coefficient β is given as the function of the Gibbs energy change of electron transfer (ΔG^0_{et}) by using Marcus theory, eqn. (2),

$$\beta = (1/2) + \Delta G^0_{et}/(8\Delta G^{\ddagger}_0) \quad (2)$$

Table 3 Observed second-order rate constants k_{obs} for the reduction of NAD^+ analogues by *trans*-[$CoMe_2(L)$] in acetonitrile at 298 K, the one-electron reduction potentials (E^0_{red} *vs.* SCE) of NAD^+ analogues, and the calculated rate constants k_{et} of outer-sphere electron transfer from *trans*-[$CoMe_2(L)$] to NAD^+ analogues

NAD^+ analogue	$E^0_{red}{}^a$/V	k_{obs}/ dm^3 mol^{-1} s^{-1}	$k_{et}{}^b$/ dm^3 mol^{-1} s^{-1}
$AcrH^+$	−0.43[c]	4.1	6×10^{-6}
3-$CNQuH^+$	−0.60	7.3×10	8×10^{-9}
3-$BrQuH^+$	−0.76	1.2×10	2×10^{-11}
QuH^+	−0.96	2.8×10^{-2}	7×10^{-15}
2-$MeQuH^+$	−1.05	3.5×10^{-4}	2×10^{-16}
4-NO_2BNA^+	−0.98	3.6×10^{-2}	3×10^{-15}
2,4-Cl_2BNA^+	−1.08[c]	1.8×10^{-2}	6×10^{-17}
4-$ClBNA^+$	−1.08[c]	6.8×10^{-3}	6×10^{-17}
BNA^+	−1.08[c]	2.6×10^{-3}	6×10^{-17}
4-$MeOBNA^+$	−1.13	3.8×10^{-3}	9×10^{-18}

[a] Determined by analysis of the cyclic voltammogram.[1,11] [b] Calculated as the maximum value for the outer-sphere electron transfer. [c] Taken from ref. 11.

where $\Delta G^{\ddagger}_0$ is the activation Gibbs energy at $\Delta G^0_{et} = 0$. Since $\Delta G^0_{et} = E^p_{red} - E^0_{red}$, from eqns. (1) and (2) the relationship between E^p_{red} and E^0_{red} [eqn. (3)] can be derived. Both E^p_{red} and $E^p_{red} - E^{p/2}_{red}$ vary depending on the sweep rate, as shown in

$$E^p_{red} = E^0_{red} - 4(1 - 2\beta)\Delta G^{\ddagger}_0 \quad (3)$$

Fig. 3. The E^p_{red} values at various sweep rates are then plotted *vs.* $4(1 - 2\beta)$ in which the β values are obtained from $E^p_{red} - E^{p/2}_{red}$ by using eqn. (1). The linear correlations are obtained as shown in Fig. 4, and agree with eqn. (3). Thus, from the intercepts of the linear plots, the E^p_{red} values of QuH^+ and derivatives are determined, as listed in Table 3.

The k_{obs} value increases generally with the positive shift in the E^0_{red} value although the k_{obs} value of 2-$MeQuH^+$ is significantly smaller than that of BNA^+ derivatives with similar E^0_{red} values.

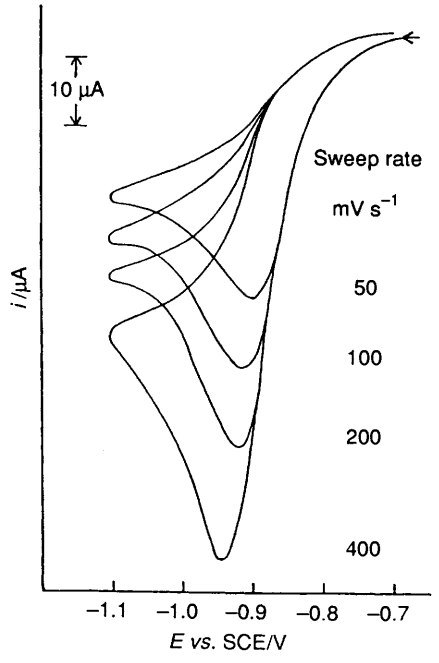


Fig. 3 Cyclic voltammograms of QuH^+ (1.0×10^{-3} mol dm^{-3}) in the presence of $NBu^n_4ClO_4$ (0.10 mol dm^{-3}) in deaerated MeCN at sweep rates 50, 100, 200 and 400 mV s^{-1}

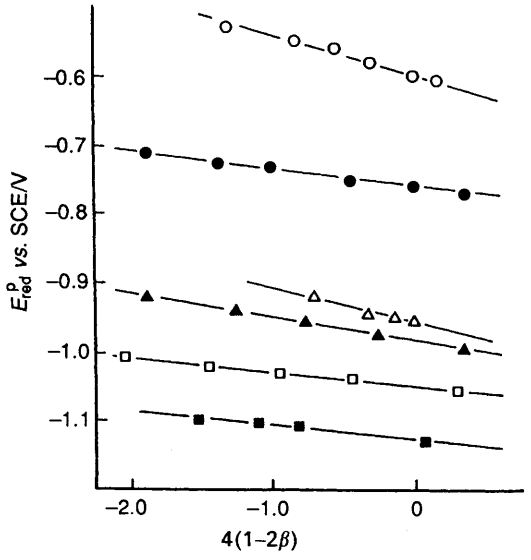
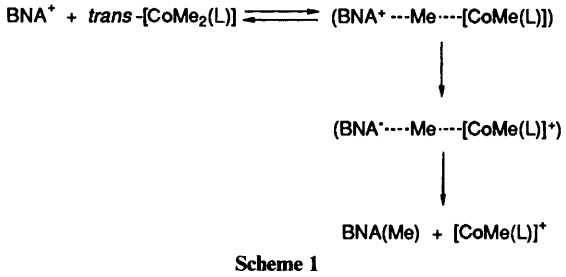


Fig. 4 The oxidation peak potentials E^p_{ox} of NAD^+ analogues: 3-$CNQuH^+$ (○); 3-$BrQuH^+$ (●); QuH^+ (△); 4-NO_2BNA^+ (▲); 2-$MeQuH^+$ (□) and 4-$MeOBNA^+$ (■), in MeCN at 298 K plotted as a function of transfer coefficient β, $4(1 - 2\beta)$



Scheme 1

With the positive shift in the E^0_{red} value electron transfer from *trans*-$[CoMe_2(L)]$ to NAD^+ analogues becomes energetically more favourable. The electron transfer from *trans*-$[CoMe_2(L)]$ to NAD^+ analogues may be highly endergonic, judging from the one-electron oxidation potential of *trans*-$[CoMe_2(L)]$ (E^0_{ox} *vs.* SCE = 0.53 V)[23] and the one-electron reduction potentials of NAD^+ analogues given in Table 3. In such highly endergonic electron transfer reactions, the maximum value of the electron-transfer rate constant (k_{et}) may be obtained by using eqn. (4), in which Z is the collision frequency, taken to be 1×10^{11} dm^3 mol^{-1} s^{-1},[24] and F is the Faraday constant. The k_{et} values thus obtained are also listed in Table 3, where the k_{obs} values are 10^6–10^{14} times greater than the k_{et} values (considered to be the maximum values for the outer-sphere electron-transfer reactions).[24] Such large discrepancies between the k_{obs} and k_{et} values may exclude an outer-sphere electron-transfer pathway, and thus the reduction of NAD^+ analogues by *trans*-$[CoMe_2(L)]$ may proceed *via* strong interaction between *trans*-$[CoMe_2(L)]$ and NAD^+ analogues. Such a reaction pathway may be viewed as a direct carbanion transfer. The carbanion (Me^-) may attack predominantly the C-2 position of X-QuH^+, where the charge density is the greatest and the C-6 position of X-BNA^+ to yield X-1,2-QuH(Me) and X-1,6-BNA(Me) as the main products, respectively (Table 1), since essentially the same regioselectivities have been reported for the hydride reduction of the NAD^+ analogues by $NaBH_4$.[13]

$$k_{et} = Z\exp[-F(E^0_{ox} - E^0_{red})/RT] \quad (4)$$

Alternatively, an inner-sphere electron transfer[25] may occur following the formation of an inner-sphere complex in which the methyl ligand bridges the carbon atom of NAD^+ analogues and [CoMe(L)], as shown in Scheme 1. Following the electron transfer, the methyl ligand may be transferred to the NAD^+ analogue. The dependence of k_{obs} on E^0_{red} (Table 3) may be ascribed to the contribution of such an inner-sphere electron-transfer pathway. The isomer distribution may be determined by the thermodynamic stability of the inner-sphere complex, which may reflect both the thermodynamic stability of the methylated products as well as the charge distribution of NAD^+ analogues. At present, however, we cannot distinguish between these two pathways: a direct carbanion transfer and an inner-sphere electron transfer. In any case, a strong interaction between the cobalt–carbon bond and NAD^+ analogues may be essential for the reaction to occur, since no reduction of NAD^+ model compounds occurs by sterically more hindered complexes, *cis*-$[CoR_2(bipy)_2]^+$, in spite of the similar E^0_{ox} values (0.63 and 0.57 V *vs.* SCE for R = Me and Et, respectively)[19] as compared with that of *trans*-$[CoMe_2(L)]$ (0.53 V *vs.* SCE).[23]

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