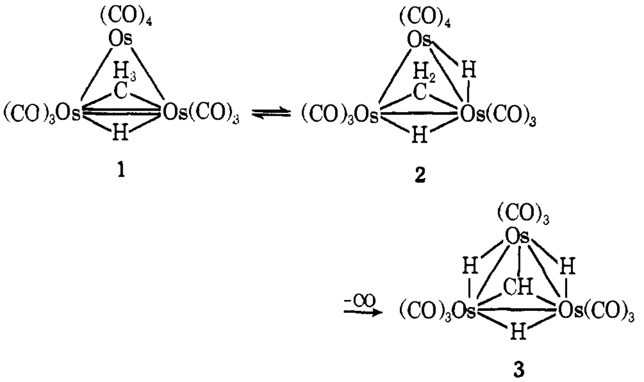
68.2 ppm ($(CD_3)_2CO$) with J_{CH} = 171 and $J_{CH'}$ = 3 Hz.

Reasonable structures may be proposed for **1**, **2**, and **3**, as shown below. Compound **3** appears entirely analogous to the previously known ethylidyne compound $H_3Os_3(CO)_9(CCH_3)$.[7]



1 2 3

The structure for **2** incorporates features displayed by $HOs_3(CO)_{10}(CHCH_2PPhMe_2)$[8] and $H_2Os_3(CO)_9(C{=}CH_2)$.[9,10] Although the ^{1}H and ^{13}C NMR signals observed for the bridging methylene in $[CpMn(CO)_2]_2CH_2$ (τ 1.35, 153 ppm)[11a] are downfield of those for **2**, the analogous signals for the terminal methylene in $Cp_2Ta(CH_3)(CH_2)$ (−0.22, 228 ppm)[11b] are even further downfield. The structure proposed for **1** is least certain but modeled after that established for $H_2Os_3(CO)_{10}$.[12] Alkyl ligands bridging two transition metals are rare, but not unknown,[13] and the upfield position of the ^{1}H NMR signal for the methyl ligand in **1** is quite distinct from the positions for the methyl groups in the series,[14] $HOs(CO)_4(CH_3)$, $HOs_2(CO)_8(CH_3)$, and $Os_3(CO)_{12}(CH_3)_2$ (all about τ 9.7).[15] Studies in progress are aimed at further characterizing the structures of **1** and **2** as well as the reactivity of all three compounds.[20]

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(15) It is interesting and perhaps significant that the methyl signal for $[(allyl)Ni(CH_3)]_2$ appears at τ 12.1, whereas the signal for $(allyl)Ni(CH_3)PMe_3$ is at 9.7.[16] Other known compounds[13] for which NMR data are available do not show a large upfield shift for the bridging alkyl but also do not involve metal centers with partially filled d shells.

The possibility that the methyl ligand in **1** is terminal but experiences an anisotropic field generated by the osmium–osmium double bond cannot be eliminated. However, we note that the terminal methyl ligands in $[WMe(NEt_2)_2]_2$, which are adjacent to a tungsten–tungsten triple bond, do not show ^{1}H (or ^{13}C) NMR signals shifted to unusually high field.[17]

Another possible explanation for the high-field signal would be a structure involving an unsymmetrical Os—C···H···Os bridge. There is a broad band at 2520 cm^{-1} in the infrared spectrum of "$Os_3(CO)_{10}(CH_4)$", both in a KBr pellet and in CCl_4 solution. However, the band does not diminish in intensity nor appear at a lower frequency in the spectrum of "$Os_3(CO)_{10}(CH_2D_2)$", which may indicate that it is a combination of $\nu_{CO} + \nu_{MC}$. The methyl ^{1}H NMR signal of **1** is somewhat broader at −80 °C than at −20 °C (relative to the internal TMS signal), but solubility problems have prevented us from operating at lower temperatures. Thus, at present there is no evidence, of the sort obtained for the molybdenum pyrazolylborate complexes,[18,18] that a C—H···Os interaction exists.

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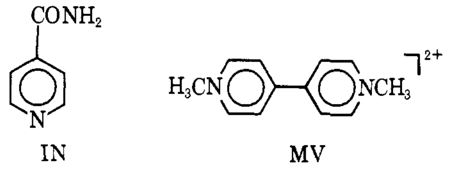
Electron Transfer. 28. A Four-Membered in Vitro Electron-Transport Chain

Sir:

Although the formal similarity between in vivo electron-transport chains and electron-transfer reactions catalyzed by an external organic species in solution has been noted,[1] the latter processes may at best be considered highly abbreviated models of the bio systems, for they involve, aside from the metal ion centers furnishing the driving force for net reaction, only a single catalytic intermediary. We here report expansion of the in vitro electron-transfer chain to four members by inclusion of two catalysts, exhibiting a combined action far more marked than the sum of their individual effects.

Table I lists the rates at which $Co(en)_3^{3+}$ is reduced by Eu^{2+} in the absence of catalysis and in the presence of isonicotinamide (IN) alone and methyl viologen (MV) alone, and in the presence of both.



IN MV

Table I. Catalyzed Reductions of $Co(en)_3^{3+}$ by Eu^{2+}, 25 °C

[Isonicotinamide], M	[Methyl viologen], M	Rate, M s^{-1} × 10^6 [a]
0	0	0.01
0.0127	0	2.3
0	5.13 × 10^{-4}	7.8
0.0127	5.13 × 10^{-4}	84

[a] Reactions were carried out in 1 M $HClO_4$: [Eu^{2+}], 0.020 M; [Co^{III}], 0.00167 M; [Eu^{3+}], 0.03 M. Reaction progress was monitored spectrophotometrically at 465 nm.[1]

Table II. Kinetic Data for the Europium(II) Reduction of $Co(en)_3^{3+}$, as Catalyzed by Combinations of Isonicotinamide and Methyl Viologen, 25 °C[a]

$[Eu^{2+}]$, M × 10^2	[IN], M × 10^2	[MV], M × 10^4	$[Eu^{3+}]$, M × 10^2	k_{obsd}[b]	k_{calcd}[c]
2.00	0	0	0	0.0008	
2.00	1.27	0	3.00	0.14	
2.00	1.20	5.13	3.00	5.0	5.0
1.00	1.20	5.13	4.00	2.7	2.6
3.00	1.20	5.13	3.00	6.9	7.7
2.00	6.00	5.13	3.00	5.0	5.0
2.00	1.71	5.13	3.00	5.0	5.0
2.00	1.20	7.70	3.00	6.9	7.7
2.00	1.20	5.13	2.00	6.9	7.7
2.00	1.20	5.13	3.00	5.0	5.0
2.00	1.20	5.13	4.00	4.0	3.8
1.33	1.20	2.57	3.00	1.9	1.7

[a] Reactions were carried out in 1 M $HClO_4$: $[Co(en)_3^{3+}]_0$, 1.67×10^{-3} M throughout. [b] Pseudo-first-order rate constants ($s^{-1} \times 10^2$) = $(-d[Co^{III}]/dt)[Co^{III}]^{-1}$. [c] k_{calcd} (in $s^{-1} \times 10^2$) = $1.5 \times 10^2[Eu^{2+}][MV][Eu^{3+}]^{-1}$ (see text).

The proposed catalytic sequence is

$$Eu^{2+} + IN \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Eu^{3+} + IN\cdot \tag{1}$$

$$IN\cdot + MV \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} IN + MV\cdot \tag{2}$$

$$MV\cdot + Co^{III} \xrightarrow{k_3} Co^{2+} + MV \tag{3}$$

In earlier studies,[1,2] k_1 has been estimated as 2.0 $M^{-1}\,s^{-1}$, k_{-1} as 5×10^5, and k_3 as 5×10^4 $M^{-1}\,s^{-1}$. The reaction of the viologen with Eu^{2+}, and that of radical IN· with $Co(en)_3^{3+}$, may be neglected in comparison with steps 1 and 3.[3] Application of the steady-state approximation to radicals IN· and MV· leads to the rate expression

$$\frac{-d[Co^{III}]}{dt} = \frac{k_1k_2k_3[IN][MV][Eu^{2+}][Co^{III}]}{k_{-1}k_{-2}[Eu^{3+}][IN] + k_2k_3[MV][Co^{III}] + k_{-1}k_3[Eu^{3+}][Co^{III}]} \tag{4}$$

From the reduction potentials of the two catalysts in this medium (IN, −0.66 V[4-7]; MV, −0.51 V[8]), k_2/k_{-2} may be calculated to be 330. Assuming that k_2, associated with a thermodynamically favored electron transfer between two conjugated organic species, exceeds 10^8 $M^{-1}\,s^{-1}$,[9] the first term in the denominator of (4) may be shown to predominate when Eu^{2+} is in excess, leading to the simplified expression

$$\frac{-d[Co^{III}]}{dt} = \frac{k_1k_2k_3[MV][Eu^{2+}][Co^{III}]}{k_{-1}k_{-2}[Eu^{3+}]} \tag{5}$$

which corresponds algebraically to the observed rate law under these conditions. Representative kinetic data are presented in Table II; note the zero-order dependence on [IN]. The ratio $k_1k_2k_3/k_{-1}k_{-2}$ is calculated to be 0.7×10^2 $M^{-1}\,s^{-1}$, which may be taken to be in reasonable agreement with our observed rate constant, 1.5×10^2 $M^{-1}\,s^{-1}$, when the large uncertainty in k_2/k_{-2} (reflecting the uncertainty in the reduction potential for IN) is considered.

With $Co(en)_3^{3+}$ in large excess, the second term in the denominator of eq 4 predominates, and the kinetic behavior of the reaction approaches that with isonicotinamide alone. Moreover, with Eu^{2+} in deficiency no inhibition by Eu^{3+} is detectable, even when $[Eu^{3+}]/[MV] = 200$, indicating that $k_2/k_{-1} \gg 200$ or that $k_2 > 10^8$ $M^{-1}\,s^{-1}$.

Both IN· and MV· react rapidly and completely with $Co(en)_3^{3+}$. The enhanced effectiveness of the two catalysts in tandem arises because MV·, the radical with the greater steady-state concentration, is generated by Eu^{2+} (necessarily by an outer-sphere path) at the lower specific rate. In effect, isonicotinamide, for which an inner sphere path is available and almost certainly preferred,[10,11] catalyzes the formation of MV·, the predominant species reacting with Co(III).

Synergism of this type is to be anticipated with other combinations of inner- and outer-sphere catalysts; varieties of both kinds have been characterized.[1,2] However, the search for an analogous three-catalyst system is expected to be less straightforward, for the combined effectiveness of the three must exceed not only the sum of the individual catalyses, but also the action of any member in conjunction with the combination of the remaining two.

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