$$R_f(\max) = R_b = \rho\sigma c\mathcal{N}/h\nu = (8\pi\nu^2\sigma\mathcal{N}/c^2)e^{-\Delta G^\circ_{B^*A}/RT_0} \quad (8)$$

at unit [B]. This is identical with eq 4 obtained kinetically. Therefore, the second law does restrict the maximum brightness S_{max} and the maximum forward rate R°_f but only in the usual way that any activation energy slows a rate. We get no new restriction from these second law arguments that we would not have recognized from ordinary transition state kinetic arguments.

Next consider the quantum yield, defined to be the number of photons per molecule which reacts. By our hypotheses, this has to be unity, since it was postulated that there was only one path, so all molecules which react must follow that path and each must give one photon. In reality there will be other paths and a certain fraction of the reacting molecules will follow them. If these competitive paths give no light, the quantum yield will drop below unity. Without explicit knowledge of the rates of the alternate paths, it is impossible to say anything further about the quantum yield, even to bound it.

These arguments show that the application of the second law to chemiluminescent reactions does not introduce any restriction on the yield or any new restrictions on the rate which would not have been recognized from normal activation energy considerations.

Acknowledgment. This work was supported by NSF grant number CHE 76 00606.

References and Notes

(1) See F. McCapra, *Q. Rev., Chem. Soc.*, **20**, 485 (1966).
(2) C. L. Perrin, *J. Am. Chem. Soc.*, **97**, 4419 (1975).
(3) J. E. Mayer in "The Luminescence of Biological Systems", F. H. Johnson, Ed., American Association for the Advancement of Science, Washington, D.C., 1955, p 48.
(4) H. Eyring, ref 3, p 244.
(5) W. Kauzmann, ref 3, p 251.
(6) Thus triplet states, vibrational entropy effects, two product molecules, transition states higher than B*, etc., could be accommodated.
(7) For induced absorption see before eq 8 below and for emission/absorption see, for example, Pauling and Wilson, "Introduction tto Quantum Mechanics", McGraw-Hill, New York, N.Y., 1935, p 301.
(8) This section is a paraphrase of the treatment of Mayer, ref 3, and is also related closely to ref 5.

E. Bright Wilson

Mallinckrodt Chemical Laboratory, Harvard University
Cambridge, Massachusetts 02138

Received January 21, 1976

Conformational Interconversion in the Formation of η^5-Cyclopentadienyl-η^3-allylmolybdenum Carbonyl Nitrosyl Cations

Sir:

The susceptibility of ligands to nucleophilic attack is greatly enhanced when the complex is cationic.[1] Thus η^5-$C_5H_5Fe(CO)_2$(olefin) cations are readily subject to attack by nucleophiles,[2] whereas neutral species, such as η^5-$C_5H_5Fe(CO)(SnR_3)$(olefin) are not.[3] Chirality as well as a localized charge can be introduced into complexes of this type by replacing CO with NO^+.[4] These reactions may be extended to chiral η^3-allyl complexes, which are potential sources of chiral stereospecifically substituted olefins.[5]

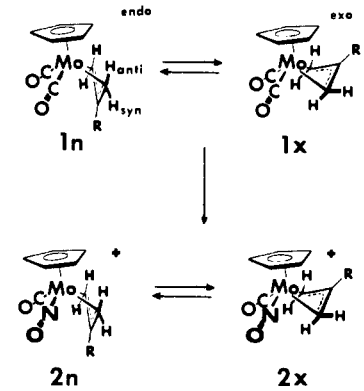
These η^5-$C_5H_5Mo(CO)(NO)$-η^3-C_3H_5 derivatives can be prepared on a large scale in high yield by reaction of the readily available dicarbonyl η^3-allyl complexes[6,7] with 1 equiv of $NOPF_6$ in acetonitrile at 0°.

$$\eta^5\text{-}C_5H_5Mo(CO)_2\text{-}\eta^3\text{-}C_3H_5 \xrightarrow[CH_3CN,\ 0^\circ]{NO^+} \eta^5\text{-}C_5H_5Mo(CO)(NO)\text{-}\eta^3\text{-}C_3H_5^+$$

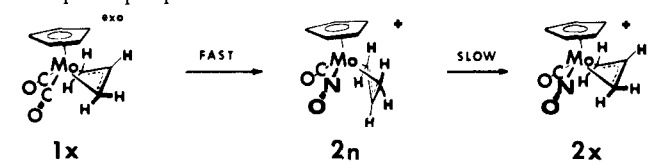
1 **2**

The reaction of η^5-$C_5H_5Mo(CO)_2(NO)$ with allyl bromide/$AgPF_6$ to produce complex **2** has been reported,[8] but the synthesis shown above provides ready access to a large number of substituted derivatives.

NMR studies suggest that **2** undergoes an intramolecular rearrangement which interconverts conformers arising from two orientations of the η^3-allyl moiety with respect to the η^5-cyclopentadienyl ring. This behavior is analogous to that observed in **1**,[6] which exists in solution as an equilibrium mixture of exo and endo conformers ($K_{exo/endo}$ = 4.7, 0°, CD_3CN). At equilibrium the conformer ratio for the nitrosyl derivative, **2**, is approximately 5.2 (0°, $(CD_3)_2CO$).



Carbonyl displacement from **1** is extremely rapid ($t_{1/2}$ < 5 s) and **2** is formed predominantly as one isomer (>85%). Two sets of syn and anti proton resonances are observed for each isomer as a consequence of the chirality at the metal.[9] Upon standing, the weaker ABCDX pattern grows in intensity and the original intense resonances shrink to 14% as the system approaches equilibrium. By analogy with **1**, the endo isomer of **2** should be less stable thermodynamically and tend to convert to the exo isomer. These intensity changes are interpreted as a kinetically controlled predominance of the endo isomer in the initial product followed by a gradual approach to an equilibrium in which the exo iomer is favored.[10] Thus, the principal path should be as follows.



It is noteworthy that the establishment of endo–exo equilibrium is over a million times faster in **1** than in **2**; i.e., the half-life at 0° is $\sim 10^{-1}$ s for **1** and $\sim 10^6$ for **2**.

Summarizing the kinetics below: two extremes which account for the reversal of conformer ratios between reactant and initial product are apparent based on the relative rates of reaction with NO^+ vs. conformational interconversion of **1**.

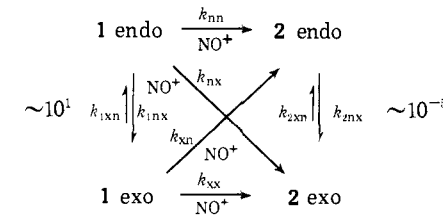


Table I. Exo/Endo Conformer Ratios at 0°

	Ligand	Reactant CH_3CN	Initial product $(CD_3)_2CO$	Final product $(CD_3)_2CO$
1,2	Allyl	4.7	0.15	5.2
3,4	2-Methylallyl	0.38	2.4	0.35

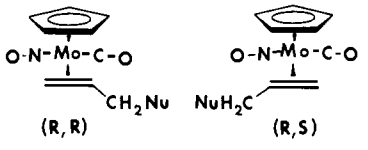
(Scheme I) The NO^+ cation reacts with **1** endo faster than with **1** exo and the endo configuration is retained. Excess **2** endo is observed because exo-endo interconversion in **1** is rapid compared to reaction with NO^+. This is consistent with $k_{1xn}[1x] > k_{nn}[NO^+][1n]$. (Scheme II) The NO^+ cation reacts rapidly compared with endo-exo interconversion in **1,** but stereoselectively interconverts configuration, e.g., **1x** → **2n.** This is consistent with $k_{xn}[NO^+] \sim k_{nx}[NO^+] \gg k_{1nx} \sim k_{1xn}$ or the formation of a common intermediate with stereoselectively decays to product.

A choice may be made between these alternatives on the basis of observations with the 2-methylallyl derivative. The endo conformer of the dicarbonyl complex, **3n,** is thermodynamically preferred due to steric interactions between the ring and the 2-methyl group ($K_{exo/endo} = 0.38$, 0°, CD_3CN). The reaction with NO^+ proceeds to yield a conformer excess in the initial product opposite to that observed in the reaction with **1.** This product distribution slowly reverses to yield a final equilibrium for the nitrosyl derivative, **4,** of $K_{exo/endo} = 0.35$. Thus opposite conformations to the allyl system predominate in the 2-methylallyl system at all stages—reactant equilibrium, initial product distribution, and final equilibrium (see Table I).

If the rate constants for reaction with NO^+ are not significantly perturbed by the methyl group, Scheme I is untenable. Since the endo conformer already predominates in the reactant in **3,** there should be a predominance of endo isomer in the initial product distribution if Scheme I were to be operative. Thus, Scheme II, which implies inversion of conformation in the major isomer upon reaction with NO^+, appears to be operative.

Since the reaction with NO^+ occurs so rapidly, it probably does not involve attack on a coordinatively unsaturated species such as η^5-$C_5H_5Mo(CO)_2$-η^1-C_3H_5 or η^5-$C_5H_5Mo(CO)$-η^3-C_3H_5. Thus it appears that a concerted SE2 attack displaces CO and interconverts allyl conformation, perhaps via a η^1-allyl. The η^1-allyl, which might be accessible from either **1x** or **1n,** might produce a product determined by the kinetic preference for re-formation of the two η^3-allyl conformers.[12]

These chiral cationic allyl complexes react with nucleophiles to produce mixtures of diastereomeric olefin derivatives. Weak stereoselectivity is shown in the addition of hydride or cyanide; however, reactions of **2** with methanol/Na_2CO_3 or sterically hindered enamines produce a single diastereoisomer.[13]



We have observed high stereoselectivity in the formation and reaction of 1-substituted and 1,3-disubstituted analogues of **2;** furthermore, it appears that asymmetric induction in olefin substituents is related to endo-exo isomer ratio. This stereoselectivity of the nucleophilic reactions may be attributed to the asymmetry in charge distribution introduced by the nitrosyl ligand. Thus, in addition to the novel "inversion" of conformation in their formation, these nitrosyls provide a system wherein asymmetric induction in nucleophilic attack appears to be dominated by an electronic rather than a steric effect.[14]

References and Notes

(1) D. A. White, *Organomet. Chem. Rev., Sect. A,* **3,** 497 (1968).
(2) D. W. Lichtenberg and A. Wojcicki, *J. Am. Chem. Soc.,* **94,** 9271 (1972); A. Rosan, M. Rosenblum, and J. Tancrede, *ibid.,* **95,** 3062 (1973); M. Rosenblum, *Acc. Chem. Res.,* **7,** 122 (1974).
(3) J. W. Faller, B. V. Johnson, and C. D. Schaeffer, Jr., *J. Am. Chem. Soc.,* **98,** 1395 (1976).
(4) H. Brunner, *Top. Current Chem.,* **56,** 67 (1975); M. T. Mocella, M. S. Okamoto, and E. K., Barefield, *Synth. React. Inorg. Metal-Org. Chem.,* **4,** 69 (1974); N. G. Connelly, *Inorg. Chim. Acta Rev.,* **6,** 47 (1972).
(5) B. M. Trost and T. J. Dietsche, *J. Am. Chem. Soc.,* **95,** 8200 (1973).
(6) J. W. Faller, C. C. Chen, M. J. Mattina, and A. Jakubowski, *J. Organomet. Chem.,* **52,** 361 (1973).
(7) R. G. Hayter, *J. Organomet. Chem.,* **13,** P1 (1968).
(8) N. A. Bailey, W. G. Kita, J. A. McCleverty, A. J. Murray, B. E. Mann, and N. W. J. Walker, *J. Chem. Soc., Chem. Commun.,* 592 (1974).
(9) Some resonances observed in the ^1H Nmr of the initial product mixture decrease with time, while others increase until equilibrium is established. The chemical shifts (in ppm downfield from Me_4Si) are as follows for cyclopentadienyl; two syn protons; and two anti protons: 2 decreasing: 6.52; 5.10, 4.30; 3.80, 3.25. 2 increasing: 6.35; 5.40, 4.90; 3.55, 3.40. 4 decreasing: 6.30; 5.05, 4.90; 3.57, 3.41. 4 increasing: 6.48, 5.00, 4.20; 3.70, 3.05.
(10) The resonances assigned to endo isomers are characterized by lower field cyclopentadienyl shifts and greater separations between the nonequivalent syn or anti protons. Confirmation of the assignments in the allyl derivative was obtained from the ^1H Nmr of the unstable η^5-indenyl-Mo(CO)(NO)-η^3-allyl cation. The major isomer in the initial product had a resonance at δ −0.15 corresponding to an endo isomer with an anti proton proximate to the indenyl ring. The minor isomer had a shift of δ 2.62 for the central proton, an upfield shift of 2.9 ppm as expected for an exo isomer.[6]
(11) This difference in interconversion rate of a factor of a million in these pseudo-seven-coordinate complexes contrast markedly with the pseudo-six-coordinate [η^5-$C_5H_5Fe(CO)$-$\eta^3C_3H_5$] analogue.[12] In the iron system, the carbonyl complex interconverts slightly slower (about a factor of three) than the nitrosyl compound (A. Rosan and J. W. Faller, unpublished). We attribute these differences to the fundamental fluxional characteristics of seven-coordinate vs. six-coordinate complexes. Both the iron and molybdenum complexes can interconvert via a η^3 to η^1 mechanism, but the pseudo-rotation path is of very low energy only for the molybdenum dicarbonyl complex.[6]
(12) J. W. Faller, B. V. Johnson, and T. P. Dryja, *J. Organomet. Chem.,* **65,** 395 (1974); R. W. Fish, W. P. Giering, D. Marten, and M. Rosenblum, *ibid.,* **105,** 101 (1976).
(13) Which pair of diastereoisomers is formed is unknown at present. An x-ray structure indicates that under some conditions the dithiocarbamate addition product has the (*R,R*)-(*S,S*) configuration;[8] however, one might anticipate that the chirality produced at the olefin metal center with **2x** might be opposite to that formed with **2n.** We are currently examining the effect of endo-exo isomerism on asymmetric induction, which can be readily studied because the ratio of exo to endo varies slowly from 0.15 to 5.2 as the system approaches equilibrium.

(14) This research was supported by the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Mobil Foundation.

J. W. Faller,* A. M. Rosan
Department of Chemistry, Yale University
New Haven, Connecticut 06520

Received January 20, 1976

Chemistry of the Macrocyclic Cobalt(II) Complex, [Co($C_{22}H_{22}N_4$)]. Reactions with Halogens, Molecular Oxygen, Alkynes, and Nitriles

Sir:

The multifarious roles of cobalt in the biochemistry of vitamin B_{12}[1,2] suggest that considerable potential still exists for the development of new chemistry with cobalt in other suitably designed ligand systems. The macrocyclic ligand, derived from the metal-template condensation of *o*-phenylenediamine with 2,4-pentanedione (see Scheme I),[3,4] is grossly distorted from planarity due to the steric interactions of the methyl groups with the benzenoid rings.[5,6] These distortions lead to a strained coordination environment for metal ions as well as activated methine carbon atoms of the ligand and may lead to unusual reactivity at either the metal or activated ligand centers, or both. The reactivity of iron(II) complexes derived from this ligand has been recently reported.[7]