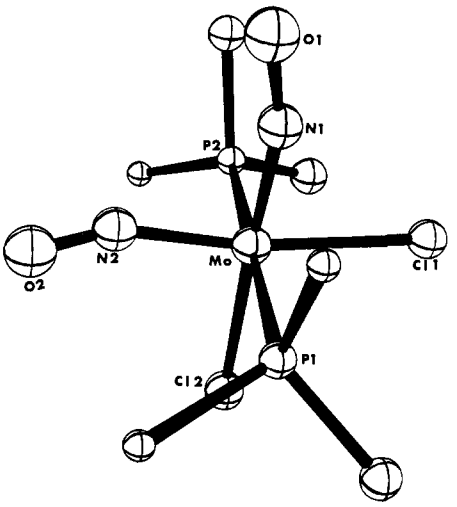

Figure 1. Structure of $Mo(NO)_2Cl_2(PPh_3)$ (only α carbons of the phenyl rings are included). Bond lengths (Å): Mo–N_1 (N_2) = 1.818 (1.905); Mo–P_1 (P_2) = 2.607 (2.584); Mo–Cl_1 (Cl_2) = 2.420 (2.477); N_1–O_1 = 1.223; N_2–O_2 = 1.158. Average estimated standard deviations: Mo–N_1 = 0.009; Mo–N_2 = 0.04; Mo–Cl = 0.008; Mo–P = 0.007; N_1–O_1 = 0.012; N_2–O_2 = 0.05.

dinitrosyl stereochemistry in favor of a trans arrangement, since a wealth of data[8] suggests trans interaction force constants are larger than those of a cis complex. A plausible alternative to this explanation, and one which is subject to experimental verification, is that $\Delta\nu$ for $Mo(NO)_2Cl_2(PPh_3)_2$ does not reflect a large interaction constant between chemically equivalent nitrosyl groups but rather is indicative of chemically distinct nitrosyls; an extreme case of this might involve one linear Mo–N–O and one bent Mo–N–O moiety. In order to definitely assign the stereochemistry of this catalyst and also to determine whether a nonlinear metal–nitrosyl linkage is present, we have completed an X-ray diffraction study of a single crystal of $Mo(NO)_2Cl_2(PPh_3)_2$.

$Mo(NO)_2Cl_2(PPh_3)_2$, prepared[7] by a bridge-splitting reaction of polymeric $Mo(NO)_2Cl_2$, was crystallized from benzene–hexane.[9] The compound was found to crystallize in space group *Cc* with a unit cell of refined dimensions a = 24.807 (34) Å, b = 9.509 (9) Å, c = 15.982 (16) Å, β = 116.0 (0.1)°, and V = 3388 Å^3. An experimental density of 1.48 g/cm^3 agreed with a calculated value of 1.47 g/cm^3 for four molecules per unit cell.

Two complete sets of independent intensity data were collected by θ–2θ scan techniques on a Picker four-circle automated diffractometer using Zr-filtered Mo Kα radiation, and 3922 reflections were independent. The structure was solved by standard Patterson and Fourier methods and refined by least-squares techniques using the 2798 reflections greater than or equal to σ. Refinement of positional and isotropic temperature parameters has converged to an R factor of 0.065. As is evident from the figure, the complex is the *cis*-dinitrosyl *cis*-dichloro isomer. This contradicts the stereochemical assignment of Beck[6] as well as that of Colton, *et al.*;[10] the latter suggested *cis*-dinitrosyl *trans*-dichloro stereochemistry on the basis of mode of formation and degree of back donation in the several isomers they isolated. Disorder, a common phenomenon in structural studies of nitrosyl complexes,[11] results in half-occupancy of each of two trans-related sites for Cl_1, N_2, and O_2 only; Cl_2, N_1, and O_1 show no evidence for this type of disorder, nor is there any evidence for a rotational disorder of NO. The nitrosyl ligands are bound to molybdenum in a distinctly nonlinear arrangement. The average[12] ∠Mo–N–O (161.8°) is too far from 120° to be considered characteristic of Lewis acid behavior, but the deviation from linearity is far greater than observed in metal carbonyls. Thus, although the theory of Kettle[13] accounts qualitatively for the bending in terms of a loss of degeneracy of π_x^* and π_y^* orbitals on NO, the increased amplitude of the bending for NO compared to CO remains to be explained. The near equality of δ(M–C–O) and δ(M–N–O) makes untenable any theory based on lower bending force constants for nitrosyl complexes.[14] On the other hand, NO is known to be a stronger π acid than CO, so that the electron population imbalance between π_x^* and π_y^* in coordinated NO will exceed that in a comparable CO complex. Deviations from linearity of ∠MNO of up to 30° observed here and elsewhere therefore seem to reflect a large and anisotropic population of the π^* orbitals and should be largest for complexes with low ν_{NO}. Studies are now underway to test this idea.

Since the nitrosyl ligands in $Mo(NO)_2Cl_2(PPh_3)_2$ are found to be chemically equivalent, the infrared anomaly remains unsolved. With accurate structural data in hand, it seems best to attribute the large dinitrosyl interaction constant, k_1, to the greater π acidity of NO relative to CO, for it is known that k_1 increases with increasing population of ligand π^* orbitals. For example, compare $C_5H_5Cr(NO)_2Cl$ ($\Delta\nu$ = 105 cm^{-1}) with $C_5H_5Fe(CO)_2Cl$ ($\Delta\nu$ = 40 cm^{-1}) or $C_5H_5Cr(NO)_2CO^+$ ($\Delta\nu$ = 94 cm^{-1}) with $C_5H_5Mn(CO)_2NO^+$ ($\Delta\nu$ = 50 cm^{-1}).

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank Climax Molybdenum Co. for gifts of $Mo(CO)_6$.

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(11) C. S. Pratt, B. A. Coyle, and J. A. Ibers, *J. Chem. Soc. A*, 2146 (1971), and references cited therein. A difference Fourier omitting only Cl_1, N_2, and O_2 showed 50% occupancy of two trans sites. Refinement was therefore continued with occupancy factors fixed at 0.5 and temperature factors identical with those of Cl_2, N_1, and O_1.
(12) ∠MoN_1O_1 = 163.1°; ∠MoN_2O_2 = 160.4°; esd = 1°.
(13) S. F. A. Kettle, *Inorg. Chem.*, 4, 1661 (1965).
(14) M. J. Cleare and W. P. Griffith, *J. Chem. Soc. A*, 372 (1969). In fact, the opposite may be true; see A. Poletti, A. Santucci, and A. Foffani, *J. Mol. Struct.*, 3, 311 (1969).

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The Use of Chiral Solvents or Lanthanide Shift Reagents to Distinguish Meso from *d* or *l* Diastereomers

Sir:

It is now well established that enantiomers may have nonidentical nmr spectra in the presence of chiral

solvents[1,2] or chiral lanthanide shift reagents.[3,4] In such chiral environments, groups which are otherwise enantiotopic by internal comparison become diastereotopic and may be anisochronous. For example, it is reported[1,5] that the methyl resonances in the pmr spectra of *N,N*-dimethylaniline oxide or of dimethyl sulfite are anisochronous when chiral 2,2,2-trifluorophenylethanol (**1**) is used as solvent. Similarly, the methyls of dimethyl sulfoxide in chiral **1** are anisochronous ($\Delta\delta$ ~0.02 ppm) and the A_3B_3 system shows a coupling of 0.4 Hz, a value previously obtained[6] from the ^{13}C satellites.[7] It should be noted that while a sample of *R*-enriched $^{13}CH_3S(=O)CH_3$ in chiral **1** shows nonequivalence in its pmr spectrum of *ca.* 0.02 ppm, no nonequivalence (*i.e.* $\Delta\delta$ <0.02 ppm) could be observed in its cmr spectrum. However, in the presence of tris[3-trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III)[4] (**2a**) or its ytterbium(III) analog **2b**, the methyl resonances of DMSO are anisochronous by both pmr and cmr. Using samples containing 0.05 mmol of substrate and 0.025 mmol of shift reagent in 0.5 ml of carbon tetrachloride, $\Delta\delta$ values for the methyls of DMSO are found to be 0.06 (pmr) and 0.20 ppm (cmr) in the presence of **2a** and 0.16 ppm (pmr) in the case of **2b**. Similarly, the enantiotopic methyls of 2-propanol, 2-propylamine, and 2-methyl-2-butanol show pmr $\Delta\delta$ values of 0.015, 0.047, and 0.020 ppm using **2a**, whereas the enantiotopic methylene protons of 2-methyl-2-butanol and 2,2-dimethylpropanol show $\Delta\delta$ values of 0.0 and 0.107 ppm (J_{AB} = 10.8 Hz), respectively.[8]

Use of chiral solvents or shift reagents to render enantiotopic groups diastereotopic *and anisochronous* can sometimes be used to distinguish meso from *dl* diastereomers. For example, in chiral **1**, the methine protons of *meso*-dimethyl 2,3-diaminosuccinate are anisochronous ($\Delta\delta$ 0.029 ppm) and hence constitute an AB system (J_{AB} = 3.7 Hz). The observation of coupling clearly distinguishes the meso from either the *d* or *l* stereoisomers (or any mixture thereof) since, *by internal comparison*, the methine hydrogens of the enantiomers are identical rather than diastereotopic in chiral media, and will show no coupling in the pmr spectrum.[9] The pesticide dieldrin (**3**) has a meso plane bisecting the C_4–C_5 bond. Hence, the hydrogens on C-4, and -5, C-3 and -6, and C-2 and -7 reside in enantiotopic environments. In the presence of shift reagent **2a**, H_3 and H_6 are anisochronous as are H_4 and H_5.

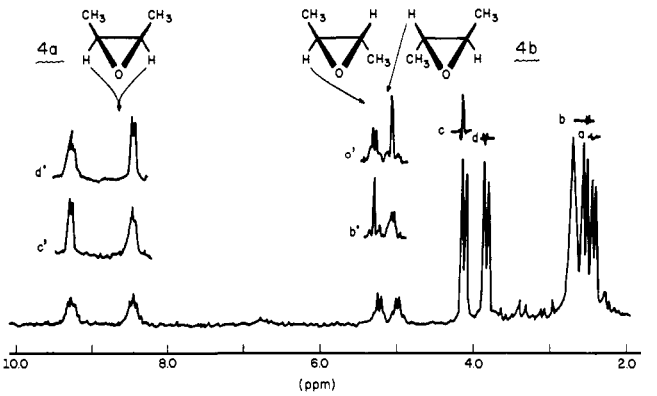
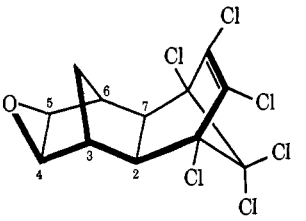


Figure 1. Pmr spectrum of a mixture of *meso*- (**4a**) and *dl*- (**4b**) 2,3-butylene oxide in the presence of europium reagent **2a**. The inset double resonance spectra were obtained by irradiating at a and observing decoupling at a′, etc. The drawings of the trans isomers (**4b**) are not meant to depict absolute configurational assignments.



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The latter show vicinal coupling ($J_{4,5}$ = 3.3 Hz) clearly demonstrating the meso stereochemistry of dieldrin.

This technique is applicable to meso–*dl* mixtures. In the presence of europium reagent **2a**, a mixture of *cis*- and *trans*-2,3-butylene oxide (**4a** and **4b**) shows four sets of methyl and methine signals, two sets from the meso isomer and one set each from the *d* and *l* isomers. Inspection of the multiplicities of the methine signals in conjunction with spin–spin decoupling experiments allows complete spectral assignment (Figure 1). It is to be noted that although the enantiomers can be differentiated, absolute configurations cannot be presently assigned. The greater overall shifts shown by the meso isomer presumably reflect the fact that one face of this isomer is more readily approached by the shift reagent than are the more highly hindered faces of the trans enantiomers.[10]

All of the preceding examples depend upon the observation of coupling between internally diastereotopic protons (in chiral environments) to distinguish meso from *dl* diastereomers. The method fails if the proton coupling is too small to observe, as might be the case were several atoms intervening. In such a situation, one might look for coupling between internally diastereotopic carbons since ^{13}C–^{13}C coupling is considerably larger than ^1H–^1H coupling and ought to better resist attenuation to zero by intervening atoms.

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(8) Since completion of this work, it has been reported by R. R. Fraser, M. A. Pettit, and M. Miskow [*J. Amer. Chem. Soc.*, **94**, 3253 (1972)] that a number of compounds containing prochiral centers show internal nonequivalence in the presence of tris[3-heptafluoroprophylhydroxymethylene-*d*-camphorato]praseodymium(III).
(9) Coupling between the methine hydrogens can also be observed, in principle, by inspection of the natural abundance ^{13}C satellites of the methine resonances. However, coupling will be observed for the *dl* as well as the meso diastereomers and they cannot be distinguished on the basis of presence or absence of coupling.
(10) Although there are little data bearing upon this point, it intuitively seems obvious that cyclic meso diastereomers will generally show greater shifts with lanthanide reagents than do the *d* or *l* diastereomers.

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Relative Stabilities of the *N*-Methyldihydropyridines[1]

Sir.

The isomeric 1,2- and 1,4-dihydropyridines have held the attention of chemists for many years.[2] This interest is due in part to the early observation[3] that the dihydropyridine ring system occurs in the ubiquitous reducing agents NADH and NADPH.[4] It was originally believed that the 1,2-dihydropyridine[3] system was present in NADH and NADPH. However, it has been shown conclusively that the isomeric 1,4-dihydropyridine occurs in these reducing agents.[5]

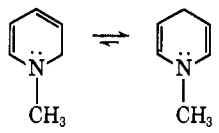
A number of methods are available for the synthesis of these ring systems and much is known about their chemistry.[2] However, there is little information available concerning their relative stabilities. There are scattered data available that indicate the 1,4-dihydropyridine system is more stable. For example, it is known that some 1,2-dihydropyridines are oxidized by silver ion at a faster rate than the 1,4 isomer[6] and Lyle and Gauthier have shown[7] that 1-methyl-3,4,5-tricyano-1,4-dihydropyridine is more stable than the isomeric 1-methyl-2,3,5-tricyano-1,2-dihydropyridine. The magnitude of this difference in stability was not reported.

In many of the previous studies on the dihydropyridine ring system and in the biological reducing agents, there are strong electron-withdrawing groups β to the nitrogen atom. The effect of these substituents on the relative stabilities of the 1,2- and 1,4-dihydropyridine systems is unknown. To date, no work has been reported on either the position or magnitude of the equilibrium between *simple* derivatives of the dihydropyridine systems.

HMO calculations[8] on the π system of the dihydropyridine ring system indicate the 1,2-dihydropyridine system is more stable.

In order to prevent problems of tautomerization we chose the *N*-methyldihydropyridines for our studies. These compounds can be prepared by reduction of the *N*-carbomethoxydihydropyridines[9] with lithium aluminum hydride. Although the dihydropyridines are relatively unstable to oxidation and polymerization they can be handled if care is used to exclude oxygen and contact with acidic surfaces.

Treatment of *either* isomer with 1.0 *M* potassium *tert*-butoxide in dimethyl sulfoxide at 91.6° produces an equilibrium mixture containing 7.7% of *N*-methyl-1,2-dihydropyridine.[10] If statistical factors are taken into



1 **2**

consideration, the *N*-methyl-1,4-dihydropyridine is 2.29 ∓ 0.01 kcal/mol more stable than the 1,2 isomer at this temperature. It is interesting to compare this result with that obtained for the carbocyclic system where 1,4-cyclohexadiene is only slightly less stable (0.07 kcal/mol with statistical correction) than 1,3-cyclohexadiene[11] at 95.0°. These results indicate that electron-withdrawing groups are not needed to stabilize the 1,4-dihydropyridine with respect to the 1,2 isomer.

It can only be speculated as to the origin of the difference in stability of these dihydropyridines. It has previously been suggested that the small difference in stability of the cyclohexadienes is due to special destabilization of the 1,3-diene. Factors such as the "cis effect"[12] and poor orbital overlap[13] have been suggested. We do not believe these effects adequately rationalize the difference in stability of the dihydropyridines. We believe that the 1,4-dihydropyridine ring system is stabilized by a favorable electronic interaction.[14] This assumption is consistent with the observation that the unsubstituted 1,4-dihydropyridine is a remarkably stable enamine.[17] In the absence of oxygen

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(12) S. Staley, Ph.D. Thesis, Yale University, 1964.

(13) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 293.

(14) Two possibilities are homoaromaticity[15] or hyperconjugation.[16]

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(17) A. G. Cook, "Enamines: Synthesis, Structure, and Reactions," Marcel Dekker, New York, N. Y., 1969.