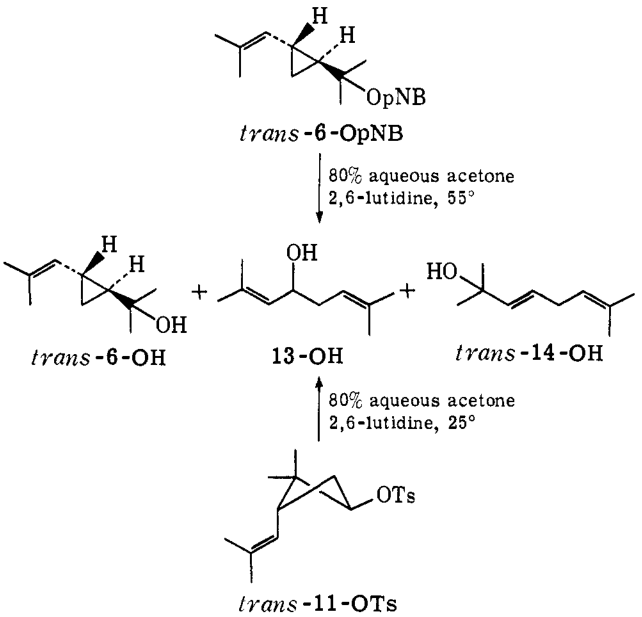
dien-4-ol (**13**-OH) (38%),[15] and *trans*-2,7-dimethyl-3,6-octadien-2-ol (*trans*-**14**-OH)[16] (60%) (Scheme IV) were formed. The allylic alcohols were also obtained in high yield by acid-catalyzed isomerization of *trans*-**6**-OH (80% aqueous dioxane, 8.8×10^{-3} *N* $HClO_4$, 62°). Although *cis*- and *trans*-**11**-OTs were not separated prior to solvolysis,[16a] the kinetics and products of *trans*-**11**-OTs could be obtained because of the large rate differential between the isomers. Hydrolysis of *trans*-**11**-OTs,[17] $k_{25°} = (3.27 \pm 0.01) \times 10^{-4}$ sec^{-1}, afforded *trans*-**6**-OH (1%), **13**-OH (36%), and *trans*-**14**-OH (63%) (Scheme IV).

Scheme IV



It is apparent that *trans*-**6**-OpNB and *trans*-**11**-OTs give products formally derived from **4** in high yield. The partial double bond between C_3 and C_4 in the allylic cation generated during solvolysis must be trans since *trans*-**14**-OH is obtained to the exclusion of its cis isomer. Parallel behavior is found during hydrolysis of chrysanthemyl derivatives where the disubstituted double bond of yomogi alcohol was found to be trans.[4a] The stereochemistry of **4** undoubtedly is a result of ionization of covalent precursors to **1**, **2**, and **3** from conformations in which the 2-methylpropenyl substituents adopt a relatively unhindered orientation and the protons at C_3 and C_4 are trans.[18] Subsequent rearrangements to the less hindered allylic isomer (*trans*-**4**) would be expected. Similar steric considerations may also be important in the enzyme-catalyzed transformations of presqualene and prephytoene pyrophosphates.[19]

The inefficient rearrangement of **1** to **4** under solvolytic conditions stands in contrast to the high yield of squalene obtained from presqualene pyrophosphate in the presence of an enzyme.[2b] We suspect that the head-to-head monoterpenes are the ultimate thermodynamic products of the rearrangement sequence. However, without a detailed knowledge of the kinetic and thermodynamic profiles of each step, we cannot choose among several possibilities by which an enzyme could assist rearrangement to **4**. Studies in this area are now in progress.

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[15] Nmr δ (CCl_4) 1.62 (6, d, allylic methyls, $J = 2$ Hz), 1.67 (6, d, allylic methyls), 1.98 (1, hydroxyl H), 2.08 (2, t, H at C_5, $J = 6.5$ Hz), 4.12 (1, d of t, H at C_4, $J_{3,4} = 8$ Hz, $J_{4,5} = 6.5$ Hz), and 4.8–5.2 ppm (2, m, H at C_3 and C_6).

[16] Nmr δ (CCl_4) 1.22 (6, s, methyls at C_2), 1.63 (6, d, allylic methyls, $J = 2$ Hz), 2.00 (1, hydroxyl H), 2.59 (2, m, H at C_5), 5.20 (1, t of sept, H at C_6, $J = 7.3$ Hz), and 5.43 ppm (2, m, H at C_3 and C_4). The assignment of stereochemistry to the disubstituted double bond was based on a strong ir band at 970 cm^{-1}.

[16a] NOTE ADDED IN PROOF. *trans*-**11**-OTs has now been obtained in >93% purity. The solvolysis results remain unchanged.

[17] *cis*-**11**-OTs could be recovered from the solvolysis mixture. Hydrolysis of *cis*-**11**-OTs in 80% aqueous acetone, $k_{50°} = (4.55 \pm 0.04) \times 10^{-5}$ sec^{-1}, gave *trans*-**6**-OH (1%), **13**-OH (59%), and *trans*-**14**-OH (40%). A rearrangement $4 \rightarrow 2$ could account for *trans*-**6**-OH.

[18] The barrier to rotation about the C_3–C_4 bond of 4 should be too high to compete with solvent collapse in aqueous solvents: P. von R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 5174 (1969).

[19] It is also interesting to note that the orientation about the C_α–C_3 bond is important in determining the geometry of the central double bond in phytoene. However, any simple interpretation is complicated by reports of both double bond isomers: G. Britton, "Aspects of Terpenoid Chemistry and Biochemistry," T. W. Goodwin, Ed., Academic Press, New York, N. Y., 1971, p 259.

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Received May 15, 1972

Nonlinear Coordination of NO in $Mo(NO)_2Cl_2(PPh_3)_2$

Sir:

Nitrosyl complexes are presently under intensive study[1] as potentially useful homogenous catalysts in a variety of reactions. Particularly intriguing is the recent report[2] that $Mo(NO)_2Cl_2(PPh_3)_2$ and related species catalyze the disproportionation of internal and α olefins, as well as the intramolecular disproportionation of α,ω-dienes. The "noninnocence" of the nitrosyl group,[3] manifested by its ability to coordinate either linearly as a Lewis base or in a bent fashion as a Lewis acid, is thought to be responsible for its efficacy in catalysis; tautomerism between base and acid behavior converts a coordinately saturated metal to a more reactive unsaturated species without the usual requirement of dissociation of a ligand. Eisenberg, *et al.*,[4] have recently synthesized $Ru(NO)_2Cl(PPh_3)_2^+PF_6^-$, which contains one linear and one bent (136°) Ru–N–O group.

In seeking an explanation for the efficiency of $Mo(NO)_2Cl_2(PPh_3)_2$ as a catalyst, we have noted infrared evidence suggestive of noninnocent behavior of the nitrosyl ligands. In particular, the large value of $\Delta\nu = \nu_{sym} - \nu_{asym}$ for $Mo(NO)_2Cl_2(PPh_3)_2$, 120 cm^{-1}, is in marked contrast to the values for a variety of *cis*-dicarbonyl complexes.[5] This anomalously large separation of ν_{sym} and ν_{asym} for $Mo(NO)_2Cl_2(PPh_3)_2$ has led others[6] to discard the original assignment[7] of *cis*-

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[1] J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, **91**, 5659 (1969); S. T. Wilson and J. A. Osborn, *ibid.*, **93**, 3068 (1971).

[2] E. A. Zuech, W. B. Hughes, D. H. Kubicek, and E. T. Kettleman, *ibid.*, **92**, 528, 532 (1970); G. C. Bailey, *Catal. Rev.*, 3, 37 (1969).

[3] C. K. Jorgensen, "Oxidation Numbers and Oxidation States," Springer-Verlag, New York, N. Y., 1969.

[4] C. G. Pierpont, D. G. Van Derveer, W. Durland, and R. Eisenberg, *J. Amer. Chem. Soc.*, **92**, 4761 (1970).

[5] Δν values for *cis*-dicarbonyl complexes range from 65 to 80 cm^{-1}: see ref 10 and J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961); L. W. Houk and G. R. Dobson, *Inorg. Chem.*, **5**, 2119 (1966); R. Colton and R. H. Farthing, *Aust. J. Chem.*, 1283 (1967).

[6] W. Beck and K. Lottes, *Chem. Ber.*, **98**, 2657 (1965).

[7] F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, 3, 1609 (1964).

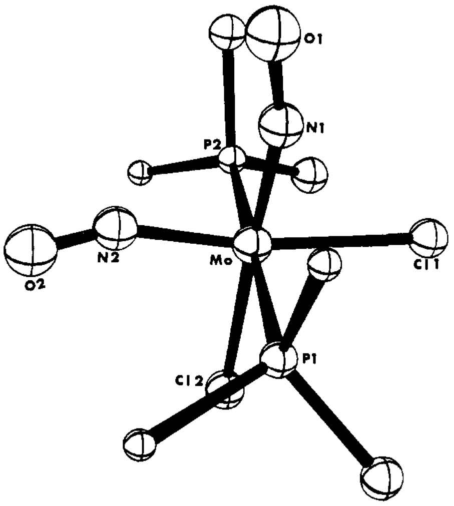

Figure 1. Structure of $Mo(NO)_2Cl_2(PPh_3)$ (only α carbons of the phenyl rings are included). Bond lengths (Å): Mo–N_1 (N_2) = 1.818 (1.905); Mo–P_1 (P_2) = 2.607 (2.584); Mo–Cl_1 (Cl_2) = 2.420 (2.477); N_1–O_1 = 1.223; N_2–O_2 = 1.158. Average estimated standard deviations: Mo–N_1 = 0.009; Mo–N_2 = 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] $\angle$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 $\angle$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_i, to the greater π acidity of NO relative to CO, for it is known that k_i 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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[8] F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

[9] Infrared analysis proved that no isomerization occurred on recrystallization.

[10] R. Colton and C. J. Rix, *Aust. J. Chem.*, **21**, 1155 (1968); M. W. Anker, R. Colton, and I. B. Tomkins, *ibid.*, **21**, 1149 (1968).

[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] $\angle MoN_1O_1$ = 163.1°; $\angle MoN_2O_2$ = 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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Received May 10, 1972

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