ture needed for thermolysis. It is necessary to invoke two such diradical species for the cis thermolyses to account for the different kinetic distribution of products when **1** and **3** are thermolyzed at the same temperature (180°). Presumably, the higher activation energy noted for rearrangement of **3** reflects the inability of the $C_5$ phenyl group to adopt the most favorable conformation for benzylic stabilization in the transition state due to steric interference from the $C_6$ phenyl group.

The results noted here demonstrate a rate instance of stereospecificity arising from slow rotation relative to ring closure in a biradical system.[14] In addition, this work may also have significance in understanding the nearly exclusive trans diphenyl stereochemistry in triplet photochemical reactions involving phenyl migration and resulting cyclopropane ring formation.[15]

**Acknowledgment.** We gratefully acknowledge support from the Merck Company, Rahway, N. J.

(14) Two instances of substituted tetramethylene diradicals having large $k_{cyc}/k_{rot}$ values have been reported: P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, 90, 5317 (1968); J. A. Berson, D. C. Tompkins, and G. Jones, *ibid.*, **92**, 5799 (1970).

(15) Reference 3 and papers cited therein.

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## Rapid Intramolecular Rearrangements in Pentacoordinate Transition Metal Compounds.[1] III. Hydridonitrosyltris(tertiary phosphine) Complexes of Ruthenium and Osmium. Synthesis, Stereochemical Nonrigidity, and Catalytic Properties[2]

*Sir:*

Transition metal nitrosyl complexes have recently found use as soluble catalysts in reactions such as olefin disproportionation[3] and hydrogenation.[4] The mode of the catalysis by these complexes may result from a facile redox process between the metal and the nitrosyl ligand which causes favorable stereochemical or structural changes about the metal.[4,5] We wish to report the synthesis of a series of nitrosyl complexes, $MH(NO)P_3$ (M = Ru, Os; P = tertiary phosphine), and studies of their stereochemical nonrigidity and catalytic properties in solution.

The complexes I–IV (Table I) are prepared in high yield by reducing the corresponding $Ru(NO)Cl_3P_2$ species[6] with refluxing ethanolic KOH in the presence of excess P. The osmium complexes V and VI are similarly prepared using 2-methoxyethanol as solvent. The deep brown crystalline compounds were characterized by elemental analysis and infrared and $^1H$ nmr spectroscopy (Table I).

The solid-state infrared spectra show absorption in the region 1900–2050 and 1600–1655 cm$^{-1}$ assignable to $\nu_{M-H}$ and $\nu_{N-O}$ modes, respectively. Deuteration of I, III, and IV (*vide infra*) causes disappearance of the $\nu_{M-H}$ mode and a shift of the $\nu_{N-O}$ to higher frequency, the magnitude and direction of which implying a resonance interaction between the $\nu_{M-H(D)}$ and $\nu_{N-O}$. This strongly indicates a trans arrangement of hydride and nitrosyl ligands[7] and the idealized ($C_{3v}$) structure A is proposed for I, III, and IV *in the solid state*[8] (Figure 1).

The $^1H$ nmr spectra of I and VI in $CH_2Cl_2$ both show a quartet to high field for the hydride resonance which is unchanged from $-100$ to $+80°$. Structure A is thus retained for I and VI in solution with $^2J_{P-H}$ also being consistent with hydride cis to the phosphine ligands.

The $^1H$ nmr of II in $CH_2Cl_2$ at 30° shows a narrow singlet for the hydride resonance and, on addition of free $PPh_2Me$, no detectable change in the spectrum occurs except for the appearance of the free phosphine resonance. Rapid *intermolecular* phosphine exchange is thus not occurring. The hydride resonance remains a singlet on cooling, but below $-90°$ broadens, and at *ca.* $-110°$ a poorly resolved 1:2:2:2:1 spectrum emerges centered at $\tau$ 15.0.[9] This low-temperature spectrum is consistent with a structure having two phosphines cis to the hydride ($^2J_{P-H} = \pm 32$ Hz) and the remaining phosphine trans or transoid to the hydride ($^2J_{P'-H} = \mp 64$ Hz). Intramolecular equilibration of the phosphine ligands[1] above $-90°$ averages the observed $^2J_{P-H}$ to zero (since $^2J_{P-H} = -{}^1/_2{}^2J_{P'-H}$) giving an apparent singlet. Similar observations[10] are found for the analogous osmium complex VI.

Of the possible idealized ($C_s$) structures for II (and VI) in solution, B, C, and D are considered the most favorable.[11]

The $^1H$ nmr spectrum of III in $CH_2Cl_2$ at 30° shows a quartet for the hydride resonance (see Figure 2). The spectrum is both solvent and temperature dependent. As the temperature is lowered, the quartet narrows (*i.e.*, the observed $^2J_{P-H}$ diminishes) but does not collapse, and concomitantly the resonance shifts downfield. Below $-48°$ however, broadening and collapse of the resonance occur.[12] These (and other[13]) observations indicate that, between $+29$ and $-48°$, two isomers[14] are populated in solution, which rapidly interconvert *via* an intramolecular process. This pro-

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(1) Part I, J. R. Shapley and J. A. Osborn, *J. Amer. Chem. Soc.*, 92, 6976 (1970); part II, D. P. Rice and J. A. Osborn, *J. Organometal. Chem.*, in press.

(2) Work supported in part by the Petroleum Research Fund, administered by the American Chemical Society.

(3) (a) E. A. Zuech, W. B. Hughes, D. H. Kubicek, and E. T. Kittleman, *J. Amer. Chem. Soc.*, 92, 528 (1970); (b) W. B. Hughes, *ibid.*, **92**, 532 (1970).

(4) J. P. Collman, N. W. Hoffman, and D. E. Morris, *ibid.*, **91**, 5659 (1969).

(5) See F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., p 573.

(6) (a) M. B. Fairy and R. J. Irving, *J. Chem. Soc. A*, 475 (1966); (b) J. Chatt and B. L. Shaw, *ibid.*, *A*, 1811 (1966).

(7) *Cf.* L. Vaska, *J. Amer. Chem. Soc.*, **88**, 4100 (1966).

(8) Similar, though not identical, shifts are also found in solution ($CH_2Cl_2$), indicating that A is appreciably populated in solution also.

(9) Since the resonance remains centered about $\tau$ 15.0 throughout, clearly no significant population of any other isomer in solution occurs.

(10) In VI, $|2{}^2J_{P-H} + {}^2J_{P'-H}|/3 = 7$ Hz, and a narrow quartet is observed down to $-50°$ at which broadening of the resonance occurs. We have not been able to obtain a satisfactory limiting spectrum, as yet.

(11) In absence of steric constraints the nitrosyl ligand would be expected to occupy an equatorial site in **TBP** or apical site in **SP** idealized geometries. B, C, and D are also consistent with the observed coupling constant data.

(12) The limiting spectrum has not yet been obtained because of solubility difficulties.

(13) Infrared studies in $CH_2Cl_2$ ($+30$ to $-25°$) show that on cooling, the band at 1990 cm$^{-1}$ increases at the expense of the 1975-cm$^{-1}$ absorption. Although separate $\nu_{N-O}$ modes have not been resolved, the envelope shifts to lower frequency on decreasing the temperature. Under identical conditions, the spectrum of I remains unchanged.

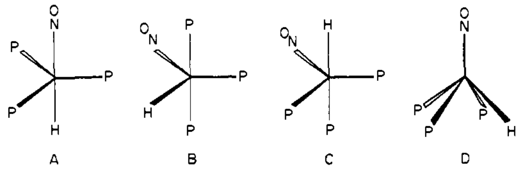
(14) Although the presence of more than two isomers in solution cannot be excluded, the nmr and ir data presently at hand can be adequately interpreted in terms of *only* two isomers, and further isomers need not be postulated at this point.

**Table I.** Infrared and $^1$H Nmr Data of the Complexes $MH(NO)L_3$

| Complex | Infrared,[a] cm$^{-1}$ | | $^1$H nmr[b] | |
|---|---|---|---|---|
| | $\nu_{M-H}$ | $\nu_{N-O}$ | $\tau$ | $^2J_{P-H}$(obsd), Hz |
| I, M = Ru; L = $PPh_3$ | 1965 (1970) | 1640[c] (1640) | 16.6 (q) | 30 |
| II, M = Ru; L = $PPh_2Me$ | 1900 (1900) | 1620 (1615) | 15.0 (s) | 0 |
| III, M = Ru; L = $PPh_2$-*i*-Pr | 1990 (1990, 1975) | 1600[c] (1600 br) | 17.2 (q) | 20 |
| IV, M = Ru; L = $PPh_2(C_6H_{11})$ | 1995 (1985, 1960) | 1600[c] (1600 br) | 17.4 (q) | 24 |
| V, M = Os; L = $PPh_3$ | 2050 (*d*) | 1635 (1620) | 17.3 (q) | 35 |
| VI, M = Os; L = $PPh_2Me$ | 1985 (1970) | 1615 (1595) | 16.5 (q) | 7 |

[a] As Nujol mulls; $CH_2Cl_2$ solution data in parentheses; br = broad. [b] Metal-hydride resonance only, measured at 30° in $CH_2Cl_2$; s = singlet, q = quartet, $^2J_{P-H}$(obsd) is the observed coupling constant. [c] In the corresponding deuterides, $\nu_{NO}$ is 1650 (I), 1625 (III), and 1630 (IV). [d] Not observed.

cess causes weighted averaging of the phosphorus-to-hydride coupling constants, $^2J_{P-H}$. The variation of the $^2J_{P-H}$(obsd) with temperature reflects the change in the relative population of these two isomers which results from changes in their free energy difference.



( P= phosphine ligand )

Figure 1. Idealized trigonal-bipyramidal (TBP) and square-pyramidal (SP) structures.

Similar observations are found using benzene as solvent, but it may be noted that (a) at a given temperature, $^2J_{P-H}$(obsd) is larger than in $CH_2Cl_2$ and (b) $^2J_{P-H}$ asymptotically approaches a value of 24.5 Hz as the temperature is raised.[15] At high temperatures, therefore, only one isomer (with $^2J_{P-H} = \pm 24.5$ Hz) is appreciably populated. A least-squares treatment of the experimental data (for $CH_2Cl_2$ solution) yields $^2J_{P-H} = \pm 1.1$ Hz ($\pm 1.0$ Hz) for the low-temperature isomer, with $\Delta H = -4.6\ (\pm 0.5)$ kcal mol$^{-1}$ and $\Delta S = -18\ (\pm 2)$ eu for the equilibrium between isomers. Structure A is proposed for the high-temperature isomer, being consistent both with the infrared[8] and coupling constant data. The small $^2J_{P-H}$ value for the low-temperature isomer indicates solution behavior identical with that observed for II, and a structure analogous to II for this isomer may be presumed. The stereochemical similarities of the isomers of III to I and II is not unexpected in view of the steric intermediacy of the isopropyl group. Further, although the considerable entropy of solvation of the low-temperature isomer (*cf.* A) could result from the enhanced solvation of a very polar TBP structure (such as B or C), the presence of D in solution would provide a most reasonable and elegant rationale of the solvation differences; *i.e.*, solutions of III (and IV[16]) involve the equilibrium

$$A(TBP) \rightleftharpoons D(SP)$$

Complexes I, III, and IV possess marked catalytic properties. At 20° in $C_6H_6$, 2.2 mmol of I isomerizes hex-1-ene (0.8 *M*) to internal olefins with a half-life of *ca.* 6 min. Under identical conditions, III and IV are similarly active. Complex II, however, isomerizes hex-1-ene at only *ca.* 4 × $10^{-3}$ times this rate. Similarly, I, III, and IV smoothly catalyze the hydrogenation of styrene,[17] while II shows negligible activity.

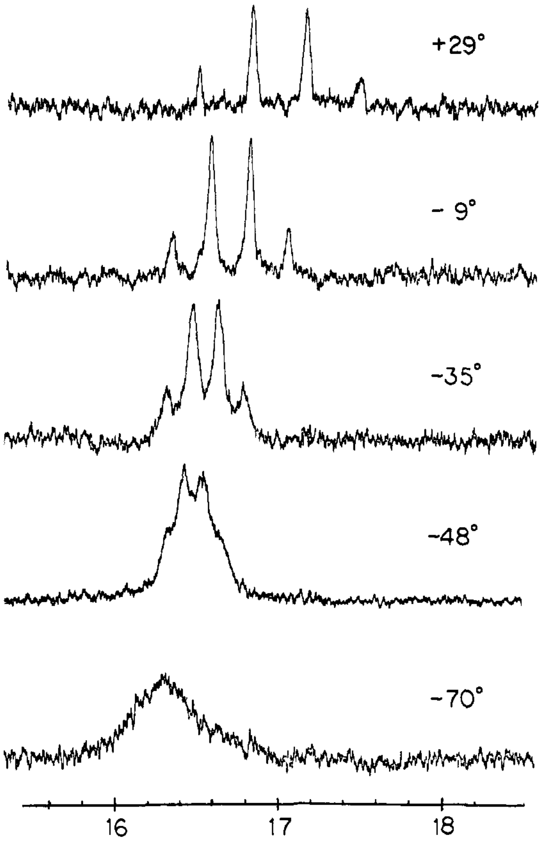


Figure 2. The temperature dependence of the hydride resonance of III in $CH_2Cl_2$ (in $\tau$ values).

Further, the deuterides of I, III, and IV are readily prepared by exchange of the hydride with deuterium gas in benzene solution, whereas II shows negligible exchange under identical conditions. Although the mechanisms of these reactions have not been elucidated, it is tempting at this point to associate the catalytic activity with the presence of isomer A in solution,

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(15) Similar behavior is also observed in $CH_2Cl_2$, but higher temperatures are needed to approach the limiting $^2J_{P-H}$ value.

(16) IV shows identical behavior with III in solution.

(17) Competitive isomerization occurs during the catalyzed hydrogenation of hex-1-ene.

with the other isomer possessing little or no activity under these conditions.

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## Critical Distance for Functional Group Interaction on Electron Impact

*Sir:*

Numerous recent studies[1–6] suggest that the electron impact induced fragmentation of organic compounds can be influenced by interaction between remote functional groups. Such interactions are demonstrated most unambiguously when they result in direct bond formation between the functional groups. In open-chain bifunctional molecules these interactions appear to be essentially independent of the distance between the two functionalities, and charge transfer with coiling of the carbon chain has been invoked.[7]

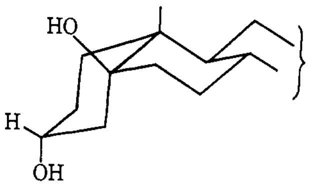
We have used the steroid molecule as a rigid template to determine how far apart two functional groups can be moved before detectable interaction ceases. A number of steroidal diols, in which both hydroxyl hydrogens had been exchanged with deuterium, were examined for loss of $D_2O$ on electron impact induced fragmentation.[8] We chose to study this particular intramolecular interaction on the basis of prior work[9] with 1,2-cyclohexanediol, in which water loss was shown to occur by a variety of paths, including significant loss of $D_2O$ (as well as $H_2O$ and HDO loss) from the dideuteroxy derivative of 1,2-cyclohexanediol.

Table I

| Steroidal diol | Loss of $D_2O$ | Closest distance O-H---OH, Å |
|---|---|---|
| 3β,17β-Dihydroxy-5α-androstane | No | 10.8 |
| 3α,12α-Dihydroxy-5β-pregnan-20-one[a] | No | 4.9 |
| 3β,6β-Dihydroxy-5α-cholestane | No | 4.7 |
| 3α,5β-Dihydroxy-5β-cholestane | No | 3.5 |
| 16α,17β-Dihydroxy-4-androsten-3-one[a] | Yes | 3.2 |
| 3β,4β-Dihydroxy-5α-cholestane | Yes | 2.4 (2.1)[b] |
| *exo,exo*-2,3-Dihydroxybicyclo[2.2.1]-heptane | Yes | 2.0 (1.4)[b] |
| 3β,5β-Dihydroxy-5β-cholestane | Yes | 1.6 (1.5)[b] |

[a] Kindly supplied by Dr. T. L. Popper, Schering Corporation, Bloomfield, N. J. [b] From measurements of Dreiding models. Numbers in parentheses are distances calculated from Δν(OH) by method of Kuhn.[11]

Our results are summarized in Table I, and we note first that no $D_2O$ loss was detected for 3β,17β-dihydroxy-5α-androstane (**1**), 3α,12α-dihydroxy-5β-pregnan-20-one (**2**), or 3β,6β-dihydroxy-5α-cholestane (**3**) as the dideuteroxy compounds. These observations reassured us that neither intermolecular deuterium transfer nor indiscriminate intramolecular scrambling of hydrogen and deuterium is a significant process under our experimental conditions. The contention that $D_2O$ loss indeed comes from direct interaction of the two OD groups and does not involve bond cleavage or scrambling was further supported by a study of 3α,5β-dihydroxy-5β-cholestane (**4**) and 3β,5β-dihydroxy-5β-cholestane (**5**) as the dideuteroxy derivatives. These compounds differ only in the configuration of the C-3 hydroxyl group, and whereas the 3β,5β-diol (**5**) lost $D_2O$, the 3α,5β-diol (**4**) did not lose $D_2O$ on electron impact. The dideuteroxy derivatives of 3β,4β-dihydroxy-5α-cholestane (**6**), 16α,17β-dihydroxy-4-androsten-3-one (**7**), and bicyclo[2.2.1]-*exo*-2,3-heptanediol (**8**) also each fragmented with loss of $D_2O$.



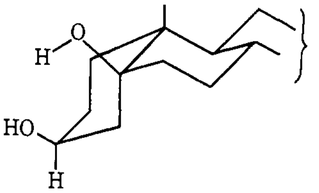


Table I shows that those compounds in our study which lose $D_2O$ on electron impact are all 1,2- or 1,3-diols, and that these diols (except for the 16α,17β-dihydroxyandrostane derivative **7**) all show strong intramolecular hydrogen bonding in solution. Also shown are the closest O-H---OH distances[10] measured from Dreiding models, as well as the O-H---OH distances calculated[11] from infrared data in solution.

The range of O-D···OD distances within which $D_2O$ loss occurs is, then, the range within which intramolecular hydrogen bonding occurs. The 16α,17β-dihydroxy steroid (**7**), for which intramolecular hydrogen bonding is neither expected nor demonstrated, is anomalous.

In conclusion, our measurements offer direct evidence that electron impact induced intramolecular interactions of functional groups will result in bond formation only when the atoms involved can be brought to within approximately normal bonding distances. This should allow other workers to assess the role played by ring opening and chain coiling in functional group interactions shown by cyclic and acyclic systems, respectively.

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[1] M. M. Green and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 5190 (1967).

[2] M. Greff, R. E. Wolff, G. H. Draffan, and J. A. McCloskey, *Org. Mass Spectrom.*, **3**, 399 (1970), and references therein.

[3] S. Sloan, D. J. Harvey, and P. Vouros, *ibid.*, in press, and references therein.

[4] J. Winkler and H. F. Grützmacher, *ibid.*, **3**, 1117 (1970).

[5] J. L. Holmes and T. St. Jean, *ibid.*, **3**, 1505 (1970).

[6] A. Guggisberg, H. J. Veith, and M. Hesse, *Tetrahedron Lett.*, 3639 (1970).

[7] J. Diekman, J. B. Thomson, and C. Djerassi, *J. Org. Chem.*, **34**, 3147 (1969).

[8] The deuterium exchange was carried out in sealed glass capillaries with $CH_3OD$, and mass spectra were measured on a CEC-110 instrument at 70 eV, using the direct inlet system at source temperatures between 160 and 230°. In all cases the mass spectrum of the nondeuterated steroidal diol was run first; then the instrument was flushed several times with $D_2O$ prior to analysis of the deuterated diol under otherwise comparable conditions. Although some $d_1$ and $d_0$ species were always present in the deuterated diols, analysis of the $M^+$ and $M - 18$ groups conclusively demonstrated $D_2O$ loss in some cases, as indicated in Table I.

[9] M. K. Strong and C. Djerassi, *Org. Mass Spectrom.*, **2**, 631 (1969).

[10] For our purposes, the O-H---OH distance is taken to be essentially the same as the O-D---OD distance for a given compound. Studies with hydrogen-bonded crystals [A. R. Ubbelohde and K. J. Gallagher, *Acta Crystallogr.*, **8**, 71 (1955)] have shown that substitution of deuterium for hydrogen produces very small changes in bond lengths. These changes are negligible compared with the errors involved in measurements from Dreiding models.

[11] $\Delta\nu(\text{OH}) = 250/d(\text{H---O}) - 74\ \text{cm}^{-1}$: L. P. Kuhn, *J. Amer. Chem. Soc.*, 74, 2492 (1952).