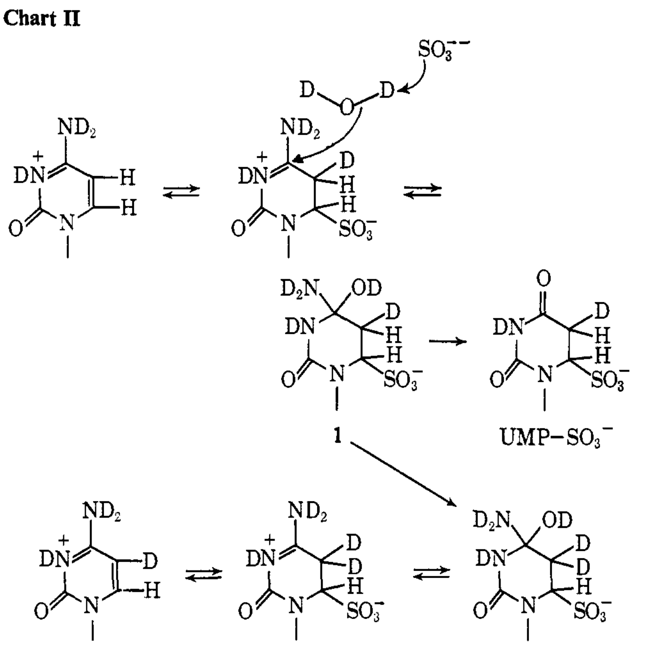
Chart II



CMP-SO$_3^-$ with sulfite, is unlikely since the disulfonate is known to be stable under similar conditions[12] and such a compound was not detected by paper chromatography and paper electrophoresis of the reaction mixture. Although it is not known whether the rate-determining step is the formation of **1** or the subsequent hydrolysis (or hydrogen exchange), the fact that the reaction is optimal at pH ~5 suggests that the protonated species of CMP-SO$_3^-$ and sulfite anion may be involved.

Previously an analogy was pointed out[4] between the bisulfite-catalyzed deamination of cytidine and the Bucherer reaction. In the Bucherer-type deamination of naphthylamine, however, the rate-determining step is the addition of bisulfite to the starting material.[20] Hydrolysis of the amino group of the resulting adduct corresponding to CMP-SO$_3^-$ is a fast step in contrast to the case of cytidine. Indeed, kinetic studies using 1-aminonaphthalene-4-sulfonic acid as the substrate have shown that the deamination rate is linear to the first order of bisulfite concentration.[21]

Comments on Mutagenesis by Bisulfite. Recently Summers and Drake[18] using bacteriophage T4 showed that the bisulfite-induced inactivation and reversion of G:C to A:T base pair are proportional to bisulfite concentration in the range of 0.18–0.9 *M*. On the basis of the results shown in Figure 2, in which the rate of deamination of CMP is approximately proportional to bisulfite concentration in the range of 0.2–3 *M*, their data appear to be consistent with the assumption that the observed rate of inactivation depends upon the rate of the bisulfite-catalyzed deamination of the cytosine residue (in T4 DNA 5-hydroxymethylcytosine is the constituent in place of cytosine).

Since $k_{\text{obsd}} = k_2K_E[s]^2/(1 + K_E[s])$, when the [s] is low enough so that $K_E[s] \ll 1$, the following correlation is obtained

$$k_{\text{obsd}} = k_2K_E[s]^2$$

In such a situation, lowering of bisulfite concentration, for instance, to 0.1 will result in a decrease of the rate of deamination of cytosine by a factor of 0.01. Hence at lower concentrations of bisulfite a proportional correlation will not be observed between the bisulfite dose and the rate of inactivation as well as that of mutation.

Acknowledgment. We thank the late Professor T. Ukita of this faculty for his encouragement, Drs. Y. Kawazoe and M. Maeda of the National Cancer Center Research Institute for valuable discussions, and Mr. K. Furihata of the Institute of Applied Microbiology, University of Tokyo, for recording the nmr spectra.

---

(20) H. Seeboth, *Angew. Chem., Int. Ed. Engl.*, 6, 307 (1967).

(21) W. A. Cowdrey and C. N. Hinshelwood, *J. Chem. Soc.*, 1036 (1946).

Communications to the Editor

Stereochemical Nonrigidity in Seven-Coordinate Trihydridorhenium Complexes

Sir:

Although magnetic equivalence of ligand nuclei in seven-, eight-, and nine-coordinate complexes has often been attributed to fluxional behavior,[1–7] only for the eight-coordinate complexes $MH_4[P(C_6H_5)_2CH_3]_4$ and $MH_4[P(C_6H_5)_2C_2H_5]_4$ (M = Mo, W)[8a] and the seven-coordinate complex $Mo(NO)(S_2CNMe_2)_3$[8b] have both limiting fast- and slow-exchange nmr spectra been detected. We now report the first observation of this for seven-coordinate hydride complexes.[9] The complexes are $ReH_3(dppe)_2$[11] (dppe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) and $ReH_3(dpae)_2$[12a] (dpae = (C$_6$-

---

(1) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, 3, 558 (1964).

(2) E. L. Muetterties, *Inorg. Chem.*, 4, 769 (1965).

(3) J. Chatt and R. S. Coffey, *Chem. Commun.*, 545 (1966).

(4) E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, 21, 109 (1967).

(5) A. P. Ginsberg, *Chem. Commun.*, 857 (1968).

(6) J. Chatt and R. S. Coffey, *J. Chem. Soc. A*, 1963 (1969).

(7) E. L. Muetterties, *Accounts Chem. Res.*, 3, 266 (1970).

(8) (a) J. P. Jesson, E. L. Muetterties, and P. Meakin, *J. Amer. Chem. Soc.*, 93, 5261 (1971); P. Meakin, L. J. Guggenberger, W. G. Peet, E. L. Muetterties, and J. P. Jesson, *ibid.*, 95, 1467 (1973); (b) R. Davis, M. N. S. Hill, C. E. Holloway, B. F. G. Johnson, and K. H. Al-Obaidi, *J. Chem. Soc. A*, 994 (1971).

(9) The complexes π-C$_5$H$_5$MoH(CO)$_2$L are formally seven-coordinate and stereochemically nonrigid. However, their permutational behavior is like that of a five-coordinate complex since in this respect the π-cyclopentadienyl group acts as if it takes up only one coordination position.[10]

(10) J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, 92, 5852 (1970).

(11) M. Freni, R. Demichelis, and D. Giusto, *J. Inorg. Nucl. Chem.*, 29, 1433 (1967).

(12) (a) A. P. Ginsberg and M. E. Tully, to be submitted for publication. (b) All ^{1}H nmr spectra were run in a ~10% CS$_2$ solution with TMS as an internal standard.

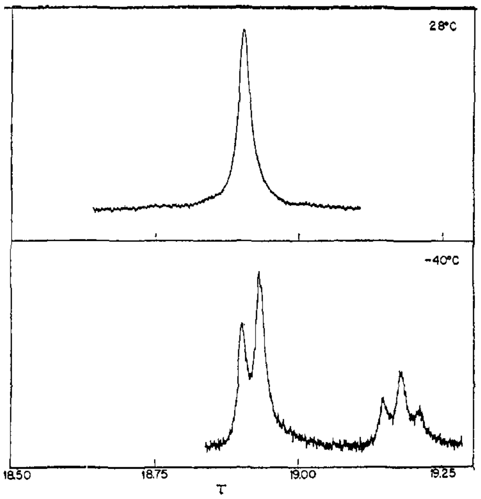


Figure 1. Hydride region 300-MHz ^1H nmr spectra of $ReH_3(dpae)_2$ at +30 and −40°.

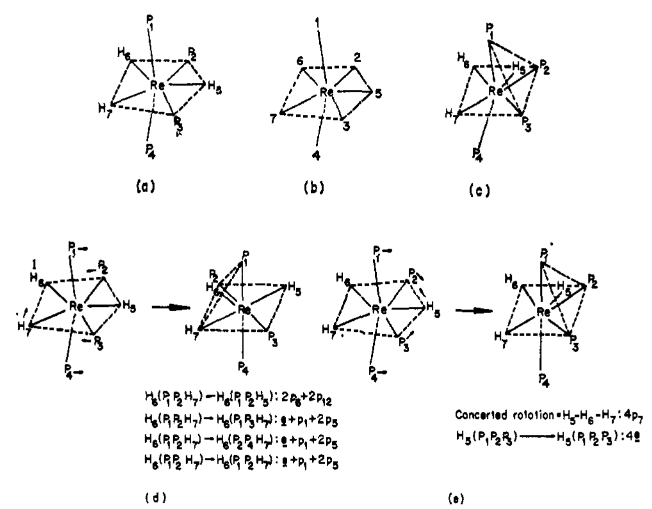


Figure 2. (a) C_{2v} "pentagonal bipyramidal" geometry of the inner coordination sphere of $ReH_3(dppe)_2$.[13] (b) Indexing of skeletal positions. (c) C_s "monocapped cis octahedral" geometry of the inner coordination sphere of $ReH_3(dppe)(PPh_3)_2$.[14] (d, e) Vibrational deformation of C_{2v} "pentagonal bipyramid" to (d) C_s monocapped trans octahedron and (e) C_s monocapped cis octahedron. Pathways for hydrogen motion in the intermediate isomer are shown by the parenthetical symbols defining the polytope faces traversed by the capping hydrogen. The implied permutational isomerization reactions follow the colon.

$H_5)_2AsCH_2CH_2As(C_6H_5)_2$). $ReH_3(dppe)(PPh_3)_2$[11] and $ReH_3(dpae)(PPh_3)_2$[12a] were also studied, but spectra of rigid forms have not been observed.

Figure 1 shows the 300-MHz ^1H nmr spectrum of the $ReH_3(dpae)_2$ hydride protons at two temperatures.[12b] The optimum low-temperature spectrum is obtained at ~−40°, and is an A_2B pattern with τ_{H_A} 18.91, τ_{H_B} 19.18 and $J_{H_A-H_B} = 9.5$ Hz. Above ~−40° the A_2B spectrum coalesces to a singlet at τ 18.87 (+30°). Below ~−40°, down to −80°, only slight line broadening is found.

$ReH_3(dppe)_2$ has a temperature dependence similar to $ReH_3(dpae)_2$. The optimum low-temperature spectrum occurs at ~−50°, and, with $^{31}P-^1H$ spin decoupling, appears as an AB_2 pattern: τ_{H_A} 17.89, τ_{H_B} 18.11, $J_{H_A-H_B} \approx 9.5$ Hz. Only a single phosphorus decoupling frequency was found. Above ~−50° the AB_2 spectrum coalesces to a singlet at τ 17.90 (+30°). The undecoupled spectrum is a quintet at +30° ($J_{P-H} = 18$ Hz) and consists of two broad multiplets with 1 : 2 intensity ratio at −50° and 300 MHz. The latter spectrum can be fitted as an AB_2X_4 spin system with $J_{H_A-P_x} = \sim 20$ Hz, $J_{H_B-P_x} = \sim 16$ Hz, and τ_{H_A}, τ_{H_B}, and $J_{H_A-H_B}$ as in the decoupled spectrum.

Contrary to the report[11] that $ReH_3(dppe)(PPh_3)_2$ shows resonances for two types of hydride hydrogens at ambient temperature, we find that the resonance of pure samples is a triplet of triplets at τ 16.74 ($J_{P_{dppe}-H} = 18$ Hz, $J_{P_{PPh_3}-H} = 24$ Hz). This is as expected for three equivalent protons coupled to two nonequivalent pairs of phosphorus atoms. The analogous dpae complex has a hydride triplet at τ 17.26 ($J_{P-H} = 26$ Hz) at +30°. Cooling to −50° has little effect on the triplet, but below −50° broadening occurs and by −93° the structure of the triplet can no longer be discerned.

On the basis of an X-ray structure determination and potential energy calculations Albano and Bellon[13] have proposed that in $ReH_3(dppe)_2$ the phosphorus and hydride hydrogen atoms form a slightly distorted pentagonal bypyramid about the rhenium (Figure 2a). In $ReH_3(dppe)(PPh_3)_2$ angle P_2–Re–P_3 is smaller than in the bis(dppe) complex by 25°, and H_5 is believed to lie above the Re, P_2, P_3 plane, surrounded by atoms P_1, P_2, and P_3.[14] The inner coordination sphere may therefore be described as a slightly distorted monocapped cis octahedron (Figure 2c).

The low-temperature spectra of $ReH_3(dppe)_2$ and $ReH_3(dpae)_2$ indicate that two of the three hydride ligands are equivalent, as expected for the Albano and Bellon structure. However, the apparent magnetic equivalence of the $ReH_3(dppe)_2$ phosphorus atoms at −50° suggests that the molecules are not yet completely rigid at that temperature. The barrier to hydride interchange is significantly lower in $ReH_3(dpae)(PPh_3)_2$ since broadening of the spectrum does not begin until the temperature is below −50°.

Combinatorial analysis by the method of Klemperer[15-17] shows that for a C_{2v} pentagonal bipyramid MH_3P_4 system there are 12 permutational isomerization reactions differentiable in a totally symmetric environment (*i.e.*, theoretically differentiable by temperature-dependent nmr line-shape simulations using the "jump model"). Let Figure 2a define the reference isomer and Figure 2b the indexing of the skeletal positions. A complete set of differentiable permutational isomerization reactions is $p_1 = (1)(2)(3)(4)(5)(67)$, $p_2 = (1)(23)(4)(5)(67)$, $p_3 = (124)(3)(5)(6)(7)$, $p_4 = (124)(3)(5)(67)$, $p_5 = (1243)(5)(6)(7)$, $p_6 = (14)(2)(3)(57)(6)$, $p_7 = (1)(2)(3)(4)(567)$, $p_8 = (124)(3)(56)(7)$, $p_9 = (124)(3)(57)(6)$, $p_{10} = (124)(3)(567)$, $p_{11} = (124)(3)(576)$, and $p_{12} = (12)(34)(57)(6)$, where the permutations operate on the indices of the skeletal positions. Interchange of nonequivalent hydrogen atoms is accomplished by p_6–p_{12}.

The fluxional behavior of $ReH_3(dppe)_2$ and $ReH_3(dpae)_2$ may be accounted for by vibrational defor-

---

[13] V. G. Albano and P. L. Bellon, *J. Organometal. Chem.*, 37, 151 (1972).

[14] V. G. Albano, P. L. Bellon, and V. Scatturin, *Ist. Lombardo Rend. Sci. A*, **100**, 989 (1966).

[15] W. G. Klemperer, *J. Chem. Phys.*, **56**, 5478 (1972).

[16] W. G. Klemperer, *Inorg. Chem.*, **11**, 2669 (1972).

[17] W. G. Klemperer, *J. Amer. Chem. Soc.*, **94**, 8360 (1972).

mation of the reference isomer to a polytopal isomer which offers a pathway for hydrogen atom interchange. Only deformations requiring relatively minor motion of the heavy atom ligands are invoked. This leads to monocapped trans and cis octahedral intermediates, *via* the deformations pictured in Figure 2d and e. A tricapped tetrahedral intermediate is unlikely because of the relatively large heavy atom motions required to reach it. The pathways for hydrogen motion and the implied permutational isomerization reactions are given beneath the intermediate polytopal isomers in Figure 2.

In the trans octahedral intermediate the capping hydrogen moves from one polytope face to another, as in the tetrahedral tunneling mechanism.[18] In the cis octahedral intermediate concerted rotation of H_5, H_6, and H_7 is possible for $\mathrm{ReH_3(dppe)(PPh_3)_2}$ and $\mathrm{ReH_3(dpae)(PPh_3)_2}$ but is blocked by the $\mathrm{CH_2CH_2}$ bridges in $\mathrm{ReH_3(dppe)_2}$ and $\mathrm{ReH_3(dpae)_2}$. The lower barrier in $\mathrm{ReH_3(dpae)(PPh_3)_2}$ may be due to the accessibility of this mechanism without initial deformation. Further work is in progress.

[18] See ref 8a and the references cited therein.

A. P. Ginsberg,* M. E. Tully
Bell Laboratories
Murray Hill, New Jersey 07974

Received March 21, 1973

Nonrigid Stereochemistry in Eight-Coordinate Pentahydridorhenium Complexes

Sir:

This communication reports the observation of slow-exchange limit nmr spectra for the stereochemically nonrigid eight-coordinate complexes $\mathrm{ReH_5(P(C_6H_5)_2C_2H_5)_3}$[1] and $\mathrm{ReH_5(As(C_6H_5)_2C_2H_5)_3}$.[2] The results are of interest because three distinct fluxional processes are frozen out between +30 and −135° and because of the information they provide about magnetic equivalence of the hydride protons in the rigid form of the molecules. Also, this represents only the second instance in which slow-exchange limit nmr spectra have been detected for nonrigid eight-coordinate complexes, the first examples being $\mathrm{MoH_4(P(C_6H_5)_2CH_3)_4}$ and $\mathrm{MoH_4(P(C_6H_5)_2C_2H_5)_4}$ and the corresponding tungsten complexes.[3]

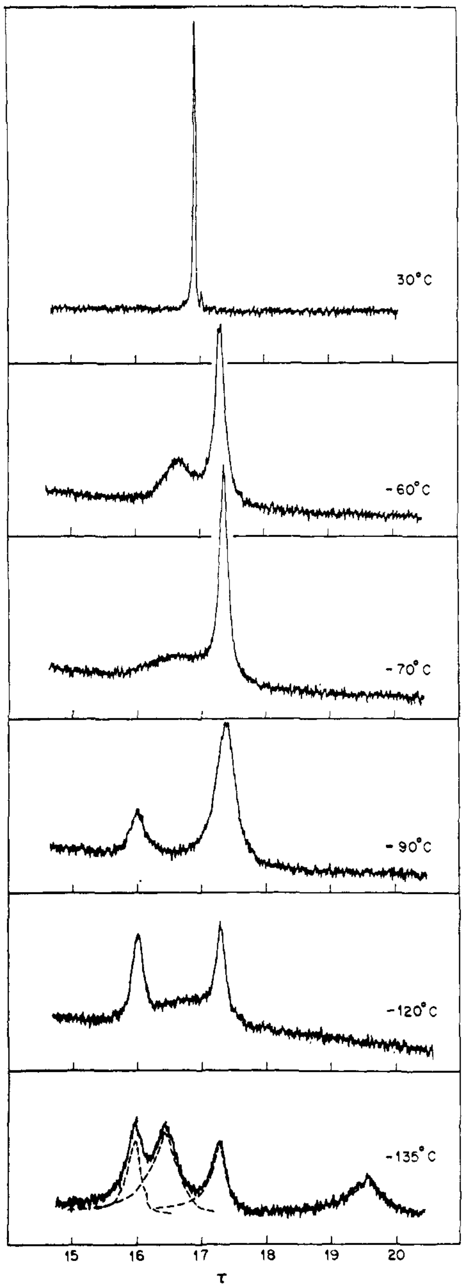


Figure 1. Hydride region 100-MHz ^1H nmr spectra of $\mathrm{ReH_5(As(C_6H_5)_2C_2H_5)_3}$ in 2:1 $\mathrm{CF_2Cl_2}$–$\mathrm{CHFCl_2}$ with TMS internal reference at several temperatures.

Figure 1 shows the hydride region 100-MHz ^1H nmr spectrum of $\mathrm{ReH_5(As(C_6H_5)_2C_2H_5)_3}$ at several temperatures. At −135° the spectrum consists of four resonances: τ 15.96, 16.42, 17.26, and 19.54; the intensities correspond respectively to 1, 2, 1, and 1 protons. On raising the temperature, the τ 16.42 and 19.54 absorptions coalesce to a single band at about the same position as the τ 17.26 band. The coalescence is complete by −90° when the spectrum consists of a composite absorption of intensity 4 protons at τ 17.39 and a band of intensity 1 proton at τ 16.00. Above −90°, the τ 16.00 resonance coalesces with the intensity 1 component of the τ 17.39 composite absorption (*i.e.*, the τ 17.26 resonance) to give at −60° a band of intensity 2 protons at τ 16.67, while the remaining intensity 3 band is now at τ 17.34. Further increase in the temperature above −60° results in coalescence of the τ 16.67 and 17.34 bands to give a single resonance of intensity 5 protons at τ 16.90 (+30°).

The spectrum of $\mathrm{ReH_5(P(C_6H_5)_2C_2H_5)_3}$, observed with ^{31}P–^1H heteronuclear spin decoupling, has a temperature dependence qualitatively similar to that of the arsenic complex. Without decoupling, the spectrum is a quartet at +30° and the quartet structure is visible down to ∼−50°. At lower temperatures, when exchange has been slowed sufficiently that nonequivalent hydrogen atoms may be distinguished, the line widths are considerably greater than in the decoupled spectra, but multiplet structure could not be seen.

Below −135°, down to ∼−155°, the lowest tem-

[1] J. Chatt and R. S. Coffey, *J. Chem. Soc. A*, 1963 (1969).
[2] A. P. Ginsberg, *Chem. Commun.*, 857 (1968).
[3] J. P. Jesson, E. L. Muetterties, and P. Meakin, *J. Amer. Chem. Soc.*, **93**, 5261 (1971); P. Meakin, L. J. Guggenberger, W. G. Peet, E. L. Muetterties, and J. P. Jesson, *ibid.*, **95**, 1467 (1973).