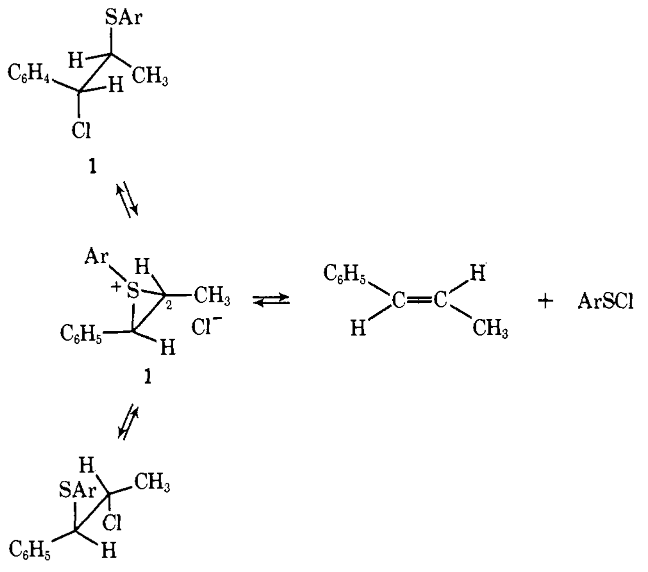
10% cyclooctene (from sulfur attack) and 90% 2-hydroxycyclooctyl 4-chlorophenyl sulfide (from carbon attack). (2) In addition to exchanging 4-chlorobenzenesulfenyl chloride with 1-octene, *erythro*-1-phenyl-1-chloro-2-propyl 4-chlorophenyl sulfide (**1**) rearranges to *erythro*-1-phenyl-2-chloro-1-propyl 4-chlorophenyl sulfide (**2**) under the same reaction conditions.[5] This rearrangement which involves attack at carbon occurs *faster* than exchange. On the basis of thermodynamic data obtained from a study of the isomerization of **1** to **2** and initial product data from the addition of 4-chlorobenzenesulfenyl chloride to *trans*-1-phenylpropene[6] we can estimate the relative rates of attack at C_1, C_2, and S of the intermediate episulfonium ion to be 120:2.4:1.0. Thus attack of carbon is preferred. This is not so surprising since the episulfonium ion formed under these conditions is probably part of an intimate ion pair with the chloride ion which can return to starting material (or its isomer) by carbon attack more easily than form the olefin by attack at sulfur. An alternate mechanism involving attack of 1-octene at the sulfur atom of the episulfonium ion seems unlikely on the basis of Helmkamp's work.



The data in Table I indicate that the structure of the 2-chloroalkyl aryl sulfide has a great effect on the time needed for exchange. These times for exchange represent two different rate processes: the rate of formation of the episulfonium ion and the relative rate of attack of sulfur. While we do not yet have the necessary rate data to quantitatively evaluate these two effects, we can note several factors which seem to be important. The ease of exchange seems to be related to the ease with which the carbon atoms of the episulfonium ion can undergo sp^2 hybridization with subsequent formation of the olefin. For the cyclic sulfides, the ease of sp^2 hybridization is in the order $9 \approx 8 > 7 \approx 5 \gg 6$ which is close to the order of the ease of exchange.[7] In addition there is a steric hindrance to attack at the backside of the episulfonium ion in the case of the nine-, eight-, and seven-membered rings which is not present in the five- and six-membered rings or the acyclic compounds. Such steric hindrance is believed to be responsible for the much slower nucleophilic ring opening of cyclooctene oxide compared to cyclohexene oxide.[8] The result is to make attack easier at sulfur relative to carbon and consequently exchange is more rapid for the cycloheptyl, cyclooctyl, and cyclononyl sulfides.

The difference in the ease of exchange between the *erythro*- and *threo*-2-chloro-1,2-diphenylethyl 4-chlorophenyl sulfide seems to be a result of eclipsing the two phenyl groups in the case of the threo isomer. Whether this effect is more important in the formation of the intermediate or in the olefin formation is currently under study.

Acknowledgment. Financial support from the National Research Council of Canada is gratefully acknowledged.

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[5] G. H. Schmid and V. M. Csizmadia, *Chem. Ind. (London)*, 1811 (1968).

[6] G. H. Schmid and V. M. Csizmadia, unpublished results.

[7] J. Sicher, *Progr. Stereochem.*, 3, 224 (1962).

[8] A. C. Cope, H. H. Lee, and H. E. Petree, *J. Amer. Chem. Soc.*, **80**, 2849 (1958).

[9] Holder of a Province of Ontario Government Fellowship, 1967–1970.

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Unusual Metalloporphyrins. VII. A Porphyrin Bridging Two Metal Atoms: μ-[Mesoporphyrin IX dimethyl esterato]bis[tricarbonylrhenium(I)]

Sir:

Metalloporphyrins other than ionic species such as those of alkali metals have been found with a single metal atom either in or slightly above the porphyrin plane.[1] Although there has been some interesting speculation on the possibility of metalloporphyrins bonded to two ligands on one side of the porphyrin plane, neither this nor any species containing as many as three "axial" ligands has ever been reported.[1] We would like to report two new metalloporphyrins which seem to illustrate additional categories of porphyrin geometry.

Equimolar quantities of mesoporphyrin IX dimethyl ester and dirhenium decacarbonyl were mixed in decalin and refluxed under argon for 2 hr. The solution was evaporated, dissolved in methanol, and chromatographed on a talc column. A small quantity of red complex, I, followed by a large quantity of brown complex, II, separated as two bands on the column.

μ-[Mesoporphyrin IX dimethyl esterato]bis[tricarbonylrhenium(I)] (I) crystallized from methanol as small dark needles, mp 250–252°, and sublimed under high vacuum at 240°. *Anal.* Calcd for $Re_2C_{42}H_{40}N_4O_{10}$: C, 44.51; H, 3.56; Re, 32.87. Found: C, 44.52; H, 3.99; Re, 32.46. The needles appeared red under a microscope and gave a red solution with visible absorptions in benzene at 519, 480 (shoulder), and 400 nm. The ir spectrum of I, both in solution (chloroform) and solid phase (KBr), has strong absorptions at 1900 and 2015 cm^{-1}. A deuteriochloroform solution gave a sharp mesoporphyrin spectrum in the pmr, thus

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[1] E. B. Fleischer, *Accounts Chem. Res.*, 3, 111 (1970).

showing the complex to be diamagnetic.[2] This is anticipated, since the proposed structure contains rhenium in the 1+ state. The lack of a high-field "hydride" resonance indicates the probable absence of a rhenium-bound hydrogen.[3]

The mass spectrum[4] of I gives further support to the above formulation. A parent peak, $(M)^+$ (*m/e* 1130),[5] was observed with a relative intensity of 43.8% compared to the $(M - 5CO)^+$ peak. In addition to several low-intensity and doubly charged peaks, an $(M - 6CO)^+$ peak was also observed (68.9%). Since naturally occurring rhenium has two common isotopes, ^{185}Re and ^{187}Re, the triplet at $(M)^+$, $(M + 2)^+$, and $(M + 4)^+$ further supports the presence of two rhenium atoms in each molecule.

(Monohydrogen mesoporphyrin IX dimethyl esterato)tricarbonylrhenium(I) (II) recrystallized as clumps of brown microcrystals from benzene–hexane. It melted at 190–192° and was distilled under vacuum at 240° onto a cold finger of the sublimation apparatus. *Anal.* Calcd for $ReC_{39}H_{41}N_4O_7$: C, 54.21; H, 4.78; Re, 21.57. Found: C, 54.93; H, 4.89; Re, 22.24. In benzene it gave a brown solution with three broad visible absorptions at 585 nm (ϵ 6.2×10^3), 485 (2.0×10^4), and 392 (1.1×10^5). Its ir spectrum was similar to that of I, having absorptions at 3380 (N–H stretch), 1900, and 2015 cm^{-1}. The proton magnetic resonance (pmr) spectrum of the brown complex was that of a complexed porphyrin with the addition of a broad ($W_{1/2}$ = 6 cps) peak at τ 14.9 corresponding to a single proton. The sharp spectrum is again indicative of a diamagnetic complex. Addition to the $CDCl_3$ solution of a small amount of DCl in D_2O caused the immediate disappearance of this peak. A comparison of the chemical shift of this exchangeable proton with that of the N–H protons in uncomplexed porphyrins (*e.g.*, τ 13.9 for mesoporphyrin)[6] leads us to believe that the proton observed here is similarly bonded to the porphyrin nitrogens. The presence of this proton would also put the rhenium atom in the 1+ state and explain the observed diamagnetism. If the proton was attached to the metal atom, we would expect the pmr absorption to occur at higher field, in the neighborhood of τ 20. By comparison, the Re–H proton of $ReH(C_5H_5)_2$ occurs at τ 23.[7]

The mass spectrum of II showed a parent peak $(M)^+$ (*m/e* 862)[8] with a relative intensity of 8.8% compared to the $(M - 3CO)^+$ peak. There were also several low-intensity and doubly charged peaks. The relative intensities of the doublet at $(M)^+$ and $(M + 2)^+$ support the presence of one rhenium atom per molecule. Further, the ratio of $(M - H)^+$ to $(M)^+$ for II is 4.5 times as large as for I. This seems to confirm, as surmised from pmr studies, the presence of a nitrogen-bonded proton in II and its absence in I.

Compound I can be prepared without significant amounts of II by using excess rhenium carbonyl and long (10 hr) reaction times. Compound II can also be prepared in similar purity by allowing stoichiometric quantities of rhenium carbonyl and porphyrin to react for a period of 1 hr.

One can convert II to I by reaction with rhenium carbonyl as in the preparation of I from porphyrin. However, attempts at the conversion of I to II by reflux in decalin with excess porphyrin were unsuccessful in periods of up to 24 hr.

On the basis of these experiments one can propose the following reaction scheme, where P represents the porphyrin dianion.

$$\tfrac{1}{2}Re_2(CO)_{10} + PH_2 \longrightarrow Re(PH)(CO)_3 \qquad (1)$$

$$Re(PH)(CO)_3 + \tfrac{1}{2}Re_2(CO)_{10} \longrightarrow (CO)_3RePRe(CO)_3 \qquad (2)$$

A single-crystal X-ray diffraction analysis will be needed to determine whether there is a metal–metal bond in I and whether the four porphyrin nitrogens are arranged to form a planar or a "puckered" ring. The latter question is significant in determining the exact arrangement of bonds between metal and porphyrin.

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(3) A. D. Buckingham and P. J. Stephens in "Nuclear Magnetic Resonance in Chemistry," B. Pesce, Ed., Academic Press, New York, N. Y., 1964, p 35.

(4) CEC 21-104 mass spectrometer.

(5) $^{185}Re_2{}^{12}C_{36}{}^{1}H_{40}{}^{14}N_4{}^{16}O_4({}^{12}C^{16}O)_6$.

(6) E. D. Becker, R. B. Bradley, and C. J. Watson, *J. Amer. Chem. Soc.*, **83**, 3742 (1961).

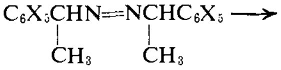
(7) B. L. Shaw, "Inorganic Hydrides," Pergamon Press, Elmsford, N. Y., 1967, p 139.

(8) $^{185}Re{}^{12}C_{36}{}^{1}H_{41}{}^{14}N_4{}^{16}O_4({}^{12}C^{16}O)_3$.

A Classical Mechanical Isotope Effect. The Effect of Ring Deuterium on the Rate of Pyrolysis of 1,1′-Diphenylazoethane

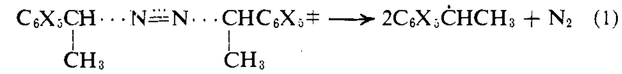
Sir:

The thermal decomposition of 1,1′-diphenylazoethane (I-H) proceeds *via* simultaneous rupture of both carbon–nitrogen bonds[1] (eq 1). We report that the kinetic isotope effect in the decomposition of ring-deuterated I-H (I-D) is nearly, if not completely, classical mechanical[2] ($\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$) in origin. To our knowledge this is the first direct measurement of $\nu_{1L}{}^{\ddagger}/\nu_{2L}{}^{\ddagger}$ at "low" temperatures.



$$\underset{\displaystyle CH_3}{C_6X_5\overset{|}{C}HN{=}N\overset{|}{C}HC_6X_5} \longrightarrow$$

I-H, X = H
I-D, X = D



$$C_6X_5\underset{\displaystyle CH_3}{CH}\cdots N\overset{\cdots}{\equiv}N\cdots\underset{\displaystyle CH_3}{CH}C_6X_5{}^{\ddagger} \longrightarrow 2C_6X_5\dot{C}HCH_3 + N_2 \qquad (1)$$

Compounds I-H and I-D were synthesized[1c] by catalytic hydrogenation of acetophenone[3] and acetophenone-d_{10}[4] azines in benzene (I-H, mp 71–72°, lit.[1c] mp 71.8–72.7°; ϵ (benzene) 45.8; λ_{max} 360 mμ), *p*-

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