would be interesting to compare $F^{19}$ n.m.r. data for additional series involving the phosphorus atom and other electronegative ligands with the results reported here. Reduced axial $\pi$-bonding is expected for ligands like –OR and $-NR_2$ since these groups each may have only one suitably oriented p orbital available for such bonding compared to the two available for fluorine.[37]

**Acknowledgment.**—The authors wish to express their appreciation to E. Anderson for performing the $F^{19}$ n.m.r. measurements and to P. Bridenbaugh for the chlorine n.q.r. measurements.

(37) Note Added in Proof.—Recent $F^{19}$ n.m.r. data [E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964)] indicate that in compounds such as $[(C_2H_5)_2N]_2PF_3$ the apical positions of a trigonal bipyramid are occupied by fluorine atoms in preference to the $(C_2H_5)_2N$ groups.

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Contribution from the John Harrison Laboratory of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

# The Dipole Moments and Structures of Disiloxane and Methoxysilane[1]

By Ravi Varma, Alan G. MacDiarmid, and John G. Miller

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The dipole moments of $(SiH_3)_2O$ and $SiH_3OCH_3$ have been measured in the gas phase and have been found to have the values 0.24 and 1.166 D., respectively. The dipole moments are discussed in relation to the structures and base strengths of the related series of ethers: $(SiH_3)_2O$, $SiH_3OCH_3$, and $(CH_3)_2O$.

The concept of $p_\pi$–$d_\pi$ bonding in the linkage between silicon and an element having at least one pair of unshared electrons has been used to explain many of the physical and chemical properties of both inorganic and organic silicon compounds.[2] It has been found to be particularly useful in rationalizing the observation that disiloxane, $(SiH_3)_2O$, has a considerably greater oxygen bond angle than its methyl analog, $(CH_3)_2O$. The fact that $(SiH_3)_2O$ is a much weaker base than $(CH_3)_2O$, even though silicon has a smaller electronegativity than carbon, is also consistent with this concept and with the observed bond angles of these ethers.

The electric dipole moments of $(SiH_3)_2O$ and $SiH_3OCH_3$ were measured in the present investigation to ascertain whether the oxygen valency angles, base strengths, and dipole moments of the related series of ethers, $(SiH_3)_2O$, $SiH_3OCH_3$, and $(CH_3)_2O$, are self-consistent and in accord with the $p_\pi$–$d_\pi$ bonding which occurs in the Si–O linkages.

## Results and Discussion

The dipole moment of gaseous $(SiH_3)_2O$ has been found to have the value of 0.24 D. The existence of a permanent moment adds to the evidence that the Si–O–Si configuration in disiloxane is bent rather than linear. Infrared spectroscopic studies[3] of disiloxane and its completely deuterated derivative show[3d] that there is a low barrier to bending through a linear configuration and that the Si–O–Si angle is roughly 150°. More recently, an electron-diffraction study[4] has found that the angle is 144.1 ± 0.9° and that the Si–O bond length is 1.634 ± 0.002 Å. Almenningen, *et al.*,[4] point out that this Si–O length corresponds to a high percentage of double-bond character in the linkage between Si and O in disiloxane, the two lone pairs on oxygen being each involved in $p_\pi$–$d_\pi$ bonding to the silicon atoms.

The bond angle 144.1 ± 0.9° and the molecular moment 0.24 D. correspond to an *effective* $\overset{+\!\!\longrightarrow}{H_3SiO}$ group moment of 0.39 ± 0.01 D. in disiloxane. Such an effective group moment is understood to contain the contribution of the lone-pair moments.[5] Due to the symmetry of the groups and of the molecule, the resultant of the lone-pair moments and the resultant of the intrinsic $\overset{+\!\!\longrightarrow}{H_3SiO}$ group moments both lie in the same direction along the same axis. They add, therefore, to form the molecular moment along that axis. This convenient situation permits combining the electron-pair moments with the intrinsic $\overset{+\!\!\longrightarrow}{H_3SiO}$ group moments to form the effective group moments, the component parts of which are not individually determinable.

The moment of gaseous $SiH_3OCH_3$ has been found to have the value 1.166 D. The Si–O–C angle de-

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(1) This report is based on portions of a thesis submitted by Ravi Varma to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This research was supported by the Advanced Research Projects Agency, Office of the Secretary of Defense.

(2) (a) F. G. A. Stone, "Hydrogen Compounds of the Group IV Elements," Prentice-Hall Inc., Englewood Cliffs, N. J., 1962; (b) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960; (c) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962; (d) E. A. V. Ebsworth, "Volatile Silicon Compounds," The Macmillan Company, New York, N. Y., 1963.

(3) (a) R. C. Lord, D. W. Robinson, and W. C. Schumb, *J. Am. Chem. Soc.*, **78**, 1327 (1956); (b) R. F. Curl and K. S. Pitzer, *ibid.*, **80**, 2371 (1958); (c) D. C. McKean, *Spectrochim. Acta*, **13**, 38 (1958); (d) J. R. Aronson, R. C. Lord, and D. W. Robinson, *J. Chem. Phys.*, **33**, 1004 (1960); W. R. Thorson and I. Nakagawa, *ibid.*, **33**, 994 (1960); D. W. Robinson, W. J. Lafferty, J. R. Aronson, J. R. Durig, and R. C. Lord, *ibid.*, **35**, 2245 (1961).

(4) A. Almenningen, O. Bastiansen, V. Ewing, K. Hedberg, and M. Traetteberg, *Acta Chem. Scand.*, **17**, 2455 (1963).

(5) J. W. Smith, "Electric Dipole Moments," Butterworths Scientific Publications, London, 1955, Chapter 5; C. A. Coulson, "Valence," 2nd Ed., Oxford Press, London, 1961, Chapter 8.

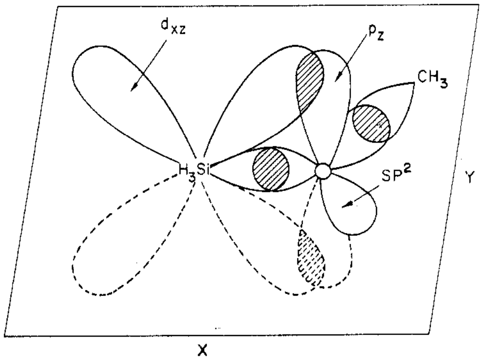

Fig. 1.—Extreme $sp^2$ hybridization and $p_\pi$–$d_\pi$ bonding in methoxysilane.

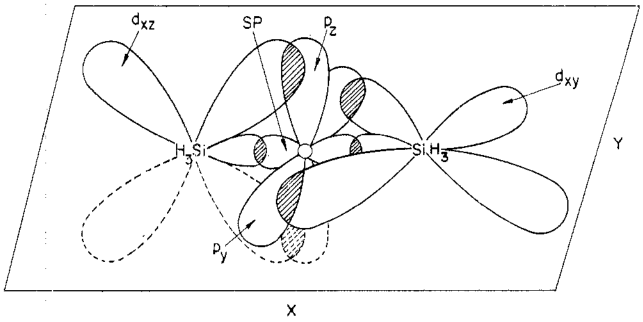

Fig. 2.—Extreme sp hybridization and $p_\pi$–$d_\pi$ bonding in disiloxane.

termined by infrared spectroscopic study[6] of this molecule and its completely deuterated derivative is close to 130°. The C–O–C angle in dimethyl ether is 111° 43′ ± 20′ by microwave spectroscopic measurement.[7] Since the dipole moment[7,8] of $(CH_3)_2O$ in the gaseous state is 1.31 D., the effective group moment of $\overset{+\!\!\longrightarrow}{\mathrm{CH_3O}}$ is 1.17 D.

If the effective moments of the $\overset{+\!\!\longrightarrow}{\mathrm{H_3SiO}}$ and $\overset{+\!\!\longrightarrow}{\mathrm{CH_3O}}$ groups were assumed to be the same in methoxysilane as in disiloxane and dimethyl ether, respectively, they would combine at the observed Si–O–C angle to produce a molecular moment of 0.967 D. This value is much too low in view of the accurate observed value, 1.166 D., and it is clear that the above assumption is not correct. Although group moment summations of this type may be carried out with many series of organic compounds (in which bond angles are relatively constant), it fails with the above series of ethers because it does not take into account the change in the contribution of the lone-pair moments with change in the hybridization of the orbitals, including the lone-pair orbitals, of the oxygen atom. Its failure may also be related to the fact that no allowance is made for any possible change in the extent of $p_\pi$–$d_\pi$ bonding in the Si–O bond in the two ethers, $CH_3OSiH_3$ and $(SiH_3)_2O$. However, this factor is probably of lesser importance.

If no $p_\pi$–$d_\pi$ bonding is present in the Si–O linkage, then regardless of whether the formal hybridization of the oxygen orbitals in these ethers is $sp^3$, $sp^2$, or sp (or intermediate between any two of these extreme forms), the resultant moment of the nonbonded electron pair moments will lie on the bisector of the M–O–M′ (M, M′ = Si or C) angle. In $sp^3$ hybridization, as for dimethyl ether, that resultant will have the maximum value; the two lone pairs, being separated by the tetrahedral angle, will give a resultant moment 1.15 times that of a single pair. In an $sp^2$ structure (see Fig. 1), the resultant moment is exactly that of a single pair, while in the sp structure (see Fig. 2), the resultant moment of the lone pairs is zero. Since the relative value of the moment of one lone pair in an $sp^3$ orbital is 1.06 times that of the lone pair in an $sp^2$ orbital,[9] it is clear that in going along the series from $sp^3$ to $sp^2$ and sp the contribution of the electron pairs to the molecular moment decreases. If $p_\pi$–$d_\pi$ bonding is present in the Si–O linkages, then the net contributions of the lone pairs of electrons to the molecular moment will be decreased. The interrelation of the hybridization of oxygen orbitals, $p_\pi$–$d_\pi$ bonding, and the basicity of the ethers can be correlated with the observed dipole moments as indicated below.

The oxygen valency angle in the series of methyl silyl ethers increases in the order $(CH_3)_2O < SiH_3OCH_3 < (SiH_3)_2O$. This indicates an increase in the amount of s-character in the oxygen $\sigma$-bonding orbitals on traversing the series. The contributions of the electrons not involved in $\sigma$-bonding to the molecular moments and base strengths can be seen qualitatively by considering certain extreme structures involving $sp^2$ or sp hybridization of the oxygen bonding orbitals. Thus, $CH_3OSiH_3$ and $(SiH_3)_2O$ lie between these two extreme types; $CH_3OSiH_3$ is closer to the $sp^2$ structure than $(SiH_3)_2O$, and $(SiH_3)_2O$ is closer to the sp structure than $CH_3OSiH_3$. Figure 1 pictures[10] $sp^2$ hybridization of the orbitals of the oxygen atom which might be expected to contribute strongly to the structure of methoxysilane as revealed by the value of 130° for the C–O–Si bond angle. As is seen by its disposition in space, one of the lone-pair orbitals enters the hybridization and contributes greatly to the molecular moment. The other lone-pair orbital, although remaining unhybridized, has good $p_\pi$–$d_\pi$ overlap with one of the d-orbitals of the silicon atom. This $\pi$-bonding will tend to decrease the intrinsic $\overset{+\!\!\longrightarrow}{\mathrm{H_3Si{-}O}}$ group moment and, hence, the molecular moment.

The above conclusions are consistent with the observations that the base strengths of the ethers decrease in the order $(CH_3)_2O > SiH_3OCH_3 > (SiH_3)_2O$.[11] Because of the overlap of the $p_z$-oxygen orbital of methoxysilane with the silicon $d_{xz}$-orbital, the electrons

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[6] E. R. Nixon and G. S. Weiss, private communication, April, 1963.

[7] U. Blukis, P. H. Kasai, and R. J. Myers, *J. Chem. Phys.*, **38**, 2753 (1963).

[8] A. A. Maryott and F. Buckley, National Bureau of Standards Circular No. 537, U. S. Government Printing Office, Washington, D. C., 1953, p. 17.

[9] See H. F. Hameka and A. M. Liquori, *Mol. Phys.*, **1**, 9 (1958). We are indebted to Professor Hameka for this information.

[10] For clarity of drawing, only one of the $sp^3$ orbitals is shown for each silicon atom and for the carbon atom in Fig. 1 and 2.

[11] C. H. Van Dyke and A. G. MacDiarmid, unpublished results (1963). Base strengths were measured in the liquid phase by a standard infrared hydrogen bonding study.

in the $p_z$-orbital will contribute less to the basicity than the lone pair of electrons in the $sp^2$ hybrid orbital which is not favorably disposed for good $p_\pi$–$d_\pi$ overlap with any of the d-orbitals of silicon.[12] In this way, the lower basicity of methoxysilane, as compared with dimethyl ether, may be explained.

Figure 2 shows sp hybridization of the orbitals of the oxygen atom that might be expected to contribute more strongly to the structure of disiloxane than to that of methoxysilane, as suggested by the observed bond angles in the compounds. In this extreme structure, neither of the lone-pair orbitals is hybridized,[2d] and neither of the lone pairs contributes to the molecular moment. This reduction in lone-pair contribution with increasing s-character of the oxygen orbitals is undoubtedly one of the chief causes of the low molecular moment of disiloxane. Also, as contributions from the lone-pair electrons decrease, *i.e.*, as the molecule approaches linearity, π-bonding will increase because of more favorable geometrical disposition of d- and p-orbitals (see Fig. 2). This will further decrease both the intrinsic moment of the $\overset{+\!\!\longrightarrow}{\mathrm{H_3Si{-}O}}$ group and the moment of the molecule. Furthermore, extensive participation of both lone pairs in $p_\pi$–$d_\pi$ bonding would lower the basicity of $(SiH_3)_2O$ to a value below that of $CH_3OSiH_3$, as is observed experimentally. The greater amount of s-character in the oxygen linkages in disiloxane would shorten the Si–O bond length and improve the $p_\pi$–$d_\pi$ overlap. This would further lower both the moment and basicity of the disiloxane. No doubt, stabilization of the sp structure results from the $p_\pi$–$d_\pi$ bonding pictured for this compound.

The same explanation probably holds for the difference of the dipole moments of $[Si(CH_3)_3]_2O$ (0.66 D. in the vapor phase[13]) and $(CH_3)_3SiOCH_3$ (1.18 D. in benzene[14]). The Si–O–Si angle in hexamethyldisiloxane has been found by electron diffraction[15] to have the value 130 ± 10°, but the Si–O–C angle in $(CH_3)_3SiOCH_3$ has not been determined.

Holland and Smyth[13] found that the atomic polarization of hexamethyldisiloxane is 7.9 cc. $mole^{-1}$. They showed that this large value gives evidence that the Si–O–Si angle in that substance is easily deformed. We have found that the atomic polarization values for disiloxane and methoxysilane are 5.06 and 2.40 cc. $mole^{-1}$, respectively. The large value for disiloxane is good evidence that the Si–O–Si angle in it is easily deformed. This is consistent with the quasilinear structure previously proposed for this compound.[3d] For the methoxysilane, the $P_A$ value is smaller and interpretation of it would be difficult because the existence of a large lone-pair moment renders uncertain the intrinsic group moment values of the vibrating groups.

## Experimental

The apparatus and techniques employed were the same as used in determining the dielectric polarization of $(SiH_3)_3N$ in the gaseous phase.[16]

Disiloxane (mol. wt. found 78.3, calcd. 78.2; vapor pressure at −63.5° found 61.8 mm., calcd.[17] 64.5 mm.; $H_2$ evolved on hydrolysis of 55.7 mg. found 96.0 ml. at N.T.P., calcd. 95.8 ml.; purity confirmed by infrared spectrum[3a]) was prepared by hydrolysis of $SiH_3I$.[18] The purity of the $(SiH_3)_2O$ was also checked after all the polarization measurements had been completed (vapor pressure at −63.6° found 61.8 mm., calcd.[17] 64.2 mm.; infrared spectrum unchanged).

Methoxysilane (mol. wt. found 62.3, calcd. 62.1; m.p. found −97.4°, lit.[19] −98.5°; vapor pressure at −63.8° found 65.2 mm., calcd.[19] 65.0 mm.; purity confirmed by infrared spectrum[19]) was prepared from $SiH_3I$ and $CH_3OH$.[19] The proton magnetic resonance spectrum of a 10% solution in carbon tetrachloride (with tetramethylsilane as internal standard) gave chemical shifts of τ 6.76 ($CH_3$) and 5.77 ($SiH_3$). The purity of the $SiH_3OCH_3$ was checked after all polarization measurements were completed (mol. wt. found 62.2; vapor pressure at −63.7° found 65.7 mm., calcd.[19] 66.0 mm.; m.p. found −97.7°; infrared spectrum unchanged).

Table I gives the molar polarization, $P$, and dipole moment, $\mu$, at different temperatures for two different samples of the disiloxane. The disiloxane was treated as a Berthelot gas in calculating the polarization from the measured dielectric constant and pressure. The values of its critical constants were taken as $p_c = 1.163 \times 10^4$ mm. and $T_c = 386.94$°K. by calculation from the boiling point[20] and the vapor pressure equation.[20] The dipole moment was calculated at each temperature by the formula $\mu = \{[P - (P_E + P_A)]\,T/6.0917 \times 10^3\}^{1/2}$, where the value of $P_E + P_A$ was obtained as the intercept value in a least-squares treatment of $P$ as a linear function of $1/T$. The $(P_E + P_A)$ values for the two samples were 27.81 and 27.54 cc. $mole^{-1}$, respectively. The values of $\mu$ scatter about the same mean value, 0.24 D., for both samples, the estimated standard deviation of the mean being ±0.005 D.

TABLE I

MOLAR POLARIZATION AND DIPOLE MOMENT OF DISILOXANE

| Sample 1 | | | Sample 2 | | |
|---|---|---|---|---|---|
| *T*, °K. | *P*, cc. | μ, D. | *T*, °K. | *P*, cc. | μ, D. |
| 299.87 | 29.047 | 0.247 | 302.54 | 28.532 | 0.222 |
| 304.48 | 28.992 | 0.243 | 311.25 | 28.785 | 0.252 |
| 312.33 | 28.798 | 0.225 | 319.30 | 28.776 | 0.254 |
| 324.61 | 28.964 | 0.248 | 324.53 | 28.822 | 0.261 |
| 327.45 | 28.763 | 0.226 | 333.60 | 28.516 | 0.231 |
| 341.09 | 28.688 | 0.222 | 346.56 | 28.383 | 0.219 |
| 354.70 | 28.834 | 0.244 | 355.47 | 28.261 | 0.205 |
| 361.44 | 28.850 | 0.248 | 361.10 | 28.833 | 0.277 |

TABLE II

MOLAR POLARIZATION AND DIPOLE MOMENT OF METHOXYSILANE

| *T*, °K. | *P*, cc. | μ, D. | *T*, °K. | *P*, cc. | μ, D. |
|---|---|---|---|---|---|
| 298.16 | 47.909 | 1.165 | 328.09 | 45.387 | 1.165 |
| 305.74 | 47.323 | 1.167 | 335.49 | 44.704 | 1.164 |
| 312.22 | 46.725 | 1.166 | 341.16 | 44.430 | 1.165 |
| 321.45 | 45.887 | 1.165 | 348.12 | 43.806 | 1.162 |
| 325.22 | 45.722 | 1.167 | 383.19 | 41.897 | 1.169 |

Table II shows the results obtained for methoxysilane by the same procedures. The values of $p_c$ and $T_c$ estimated from the

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[12] See R. West, L. S. Whatley, and K. J. Lake, *J. Am. Chem. Soc.*, **83**, 761 (1961).

[13] R. S. Holland and C. P. Smyth, *ibid.*, **77**, 268 (1955).

[14] K. Matsumura, *Bull. Chem. Soc. Japan*, **35**, 801 (1962).

[15] K. Yamasaki, A. Kotera, M. Yokoi, and Y. Ueda, *J. Chem. Phys.*, **18**, 1414 (1950); M. Yokoi, *Bull. Chem. Soc. Japan*, **30**, 100, 106 (1957).

[16] R. Varma, A. G. MacDiarmid, and J. G. Miller, *J. Chem. Phys.*, **39**, 3157 (1963).

[17] A. Stock, C. Somieski, and R. Wintgen, *Ber.*, **50**, 1754 (1917).

[18] H. J. Emeléus, A. G. MacDiarmid, and A. G. Maddock, *J. Inorg. Nucl. Chem.*, **1**, 194 (1955).

[19] B. Sternbach and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **83**, 3384 (1961).

[20] R. Wintgen, *Ber.*, **52**, 724 (1919).

vapor pressure equation[19] and boiling point[19] were 4.25 × $10^4$ mm. and 378.89°K. The $P_E + P_A$ sum was 20.19 cc. $mole^{-1}$. The mean value of the dipole moment of methoxysilane is 1.166 D., the estimated standard deviation of this mean being ±0.0004 D.

The mean of the least-squares values of $P_E + P_A$ for disiloxane is 27.68 cc. $mole^{-1}$. The electronic polarization, $P_E$, estimated from the bond refraction values,[21] 3.17 and 1.80, for Si–H and Si–O is 22.62 cc. $mole^{-1}$, which gives $P_A$ = 5.06 cc. $mole^{-1}$. For methoxysilane, the group and bond refraction values, Si–O–$CH_3$ = 8.284[2b] and Si–H = 3.17,[21] gave $P_E$ = 17.79 cc. $mole^{-1}$, so that $P_A$ = 2.40 cc. $mole^{-1}$.

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[21] A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954).

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CONTRIBUTION FROM THE RESEARCH LABORATORIES,
ETHYL CORPORATION, FERNDALE 20, DETROIT MICHIGAN

# The Addition of Dicyclopentadienylrhenium Hydride to Some Acetylenes

BY MICHAEL DUBECK AND RAYMOND A. SCHELL

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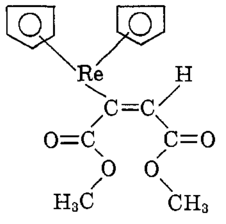
Dicyclopentadienylrhenium hydride reacts with dimethylacetylene dicarboxylate to form a dicyclopentadienylrhenium-substituted dimethyl maleate. Methyl propiolate reacts similarly to yield a dicyclopentadienylrhenium-substituted acrylate. The maleate–rhenium complex can be readily isomerized to the fumarate form with platinum. Hydrogenation of the maleate over platinum produces a cyclopentylcyclopentadienylrhenium-substituted dimethyl fumarate.

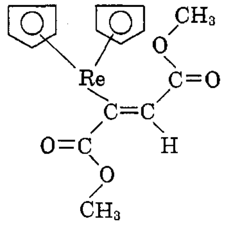
In contrast to a number of studies on the reactions of transition metal carbonyls and their derivatives with acetylenes,[1,2] the behavior of the transition metal cyclopentadienyls has received little published attention. Of the latter class of compounds, only dicyclopentadienylnickel is known to yield stable products with acetylenes.[3] Our present studies in this area of transition metal derivatives not containing carbonyls show that dicyclopentadienylrhenium hydride reacts with some acetylenes to form novel products.

## Results

Dicyclopentadienylrhenium hydride reacts almost instantaneously with dimethylacetylene dicarboxylate in tetrahydrofuran at room temperature. The reaction will also occur in other solvents, such as diethyl ether, but at a reduced rate. The resulting product has been assigned a structure corresponding to a dicyclopentadienylrhenium-substituted dimethyl maleate (I). Treatment of the maleate-type complex with platinum in benzene at 70° readily transforms it into the corresponding geometric isomer II. Although both complexes possess very similar infrared spectra, II is bright red in color as opposed to a dark amber-red for I. Both complexes possess similar chemical properties, being unstable in air but inert toward water. However, solubilities in organic solvents differ markedly—I is quite soluble in diethyl ether, benzene, and methanol, whereas the isomer II exhibits only slight solubility in ether and is moderately soluble in benzene and methanol. As is characteristic of dicyclopentadienylrhenium hydride, the complexes I and II behave as bases. They can be extracted from organic solvents, such as benzene or diethyl ether, with 10% aqueous sulfuric acid and are reliberated into the organic phase by neutralizing the acid.



I

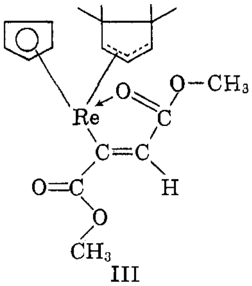


II

In an attempt to determine the stability of these materials to strong acid, a solution of I in 10% aqueous sulfuric acid was allowed to stand for 18 hr. The acid was then neutralized and I was extracted from the aqueous phase and crystallized from diethyl ether, with a recovery of approximately 50%. This observation illustrates the remarkable inertness of this particular rhenium–carbon σ-bond to protolytic attack.

Hydrogenation of I over platinum in ethanol at atmospheric pressure and room temperature yields an extremely dark red diamagnetic complex for which structure III is assigned and which corresponds to a cyclopentenylcyclopentadienylrhenium-substituted dimethyl fumarate. A strong coordinate bond exists between the *cis* carbonyl group and rhenium.

Compound III exhibits oxidative instability similar



III

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[1] M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).

[2] P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, **1**, 511 (1962).

[3] M. Dubeck, *J. Am. Chem. Soc.*, **82**, 502 (1960); *ibid.*, **82**, 6193 (1960).