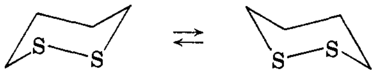
If the interchange from one isomer to the other



is treated as a typical rate process, and the transmission coefficient is equal to unity, then Eyring's equation gives $\Delta F = 11.6$ kcal./mole. Thus the molecular conformations have a very short lifetime. Even at −43° the half-life for the enantiomers is only 0.02 sec.

Rotatory dispersion in a disulfide absorption band indicating the asymmetry resulting from restricted rotation about the disulfide bond has indeed been observed in substances containing another asymmetric-inducing center.[5]

The same measurements on cyclohexane[6] with similar assumptions give a value of 9.7 kcal./mole for ΔF^*. If the six-membered rings are inverted by passing through intermediate boat forms, only one methylene opposition is involved in the transition through the maximum barrier in dithiane as compared to four in cyclohexane. Thus, one estimation of the ΔF^* for disulfide rotation alone (in the cyclic compound) might be about 9.2 kcal./mole. Since the maximum dihedral angle in the six ring is likely to be about 60°, the energy difference (ΔF^*) between 0° and 90° (assuming a cos dependence[7]) would be 12.3 kcal./mole. The entropy of activation (ΔS^*) for this reaction is, however, not known, and we must await a direct measurement of the temperature coefficient to evaluate the heat term.[8] Since the entire transition in the spectrum from a single line to a quadruplet occurs between −40 and −50°, precise temperature control and simpler spectra would be desirable. Experiments toward this end are in progress.

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[5] C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Company, Inc., New York, N. Y., 1960, p. 223.

[6] F. R. Jensen, D. S. Noyce, C. H. Sederholm and A. J. Berlin, THIS JOURNAL, **82**, 1256 (1960).

[7] W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry," ed. by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 55.

[8] D. W. Scott, H. L. Finke, M. E. Gross, G. R. Guthrie and H. M. Huffman, THIS JOURNAL, **72**, 2424 (1950); D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, R. E. Pennington and G. I. Waddington, *ibid.*, **74**, 2478 (1952); G. Bergson and L. Schotte, *Arkiv. Kemi*, **13**, 43 (1958).

[9] Postdoctoral Fellow 1959–1960. On leave of absence from the University of Uppsala, Uppsala, Sweden. Appointment supported by the International Cooperation Administration under the Visiting Research Scientists Program administered by the National Academy of Sciences of the United States of America.

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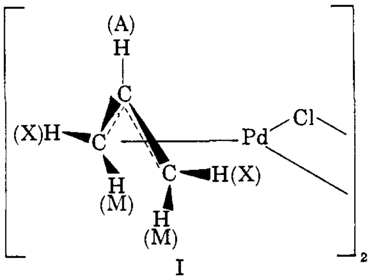
RECEIVED JUNE 23, 1960

STRUCTURES OF THE ALLYL AND CROTYL PALLADIUM CHLORIDE COMPLEXES

Sir:

The allylpalladium chloride (I) and crotylpalladium chloride (II) complexes[1] are unusually stable for organometallic halides. Our nuclear magnetic resonance (n.m.r.) results favor a non-classical structure for each compound.[2] Infrared spectra also support these assignments.

The 60-mc. spectrum shows that I has three types of protons in the ratio of 1:2:2. Several structures can be eliminated immediately. The structure with the allyl group σ-bonded to Pd should have four types of protons. The structure which has an additional π-Pd bond should have four or five different kinds of protons. Also excluded is the possibility of rapid allylic rearrangement observed[3] for allylmagnesium bromide which has only two types of protons. The structure consistent with the observed n.m.r. spectrum is the non-classical one shown where the dotted lines are electron deficient bonds.



I

In the calculation of the AM_2X_2 system, all off-diagonal matrix elements between Ψ_m and Ψ_n were neglected when they differed in any of the total spin components $F_z(A)$, $F_z(M)$ or $F_z(X)$ because the chemical shifts between protons were many times greater than the coupling constants. At 60 mc. the spectra parameters in c.p.s. are

$$\delta_A = 52.5,\ \delta_M = 135.2,\ \delta_X = 197.4$$

$$|J_{AM}| = 6.4,\ |J_{AX}| = 12.8 \text{ and } |J_{MX}| \approx 0$$

The corresponding values obtained at 15.1 mc. are

$$\delta_A = 13.0,\ \delta_M = 33.8\ \delta_X = 51.0$$

$$|J_{AM}| = 6.5,\ |J_{AX}| = 12.9 \text{ and } |J_{MX}| \approx 0$$

From the 60-mc. spectrum of II it is clear that one of the X-protons has been replaced by the methyl group. In place of the 135.2–c.p.s. doublet in I, resulting from the two equivalent M-protons, is now a group of peaks centered at 146 c.p.s. produced by protons M and M′. (The M′ proton and the methyl group are bonded to the same carbon atom.) The total area is still equivalent to two protons. The nuclear system excluding the methyl group is considered to be AMM′X. The spectra parameters in c.p.s. are

$$\delta_A = 57.9,\ \delta_{M'} = 146.1,\ \delta_M = 143.1,\ \delta_X = 209.7$$

$$\delta_{CH_3} = 299,\ |J_{AM}| = 6.3,\ |J_{AM'}| = 12.0$$

$$|J_{AX}| = 11.5,\ |J_{M'CH_3}| = 6.0, \text{ and } |J_{MX}| \approx 0$$

The protons M and X bonded to the same carbon atom in I differ by 62.2 c.p.s. in their chemical shift values. A similar large difference of 40.2 c.p.s. between the α- and the β-protons in the C_5H_6 ring was observed in $(\pi\text{-}C_5H_5)(C_5H_6)Co$.[4] Hα, which has a higher chemical shift value than Hβ, is on the

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[1] J. Smidt and W. Hafner, *Angew. Chem.*, **71**, 284 (1959).

[2] A Varian Associates 60-mc. and 15.1-mc. high resolution n.m.r. spectrometer and a Beckmann IR-7 spectrometer were used in this work. All solutions were 10% in $CDCl_3$. The n.m.r. peaks were referred to an external benzene standard. The complexes I and II were prepared as described previously[1] and gave correct analyses.

[3] J. E. Norlander and J. D. Roberts, THIS JOURNAL, **81**, 1769 (1969).

[4] M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959).

side of the C_5H_6 ring nearer to the metal atom. By analogy, it is suggested that the X-protons lie closer to Pd than the M-protons in I as illustrated perspectively above. The bond between the allyl group and Pd is delocalized, somewhat analogously to the π-cyclopentadiene–metal bond in metallocenes. However, in contrast to the metallocenes, the allyl carbons do not have the same unpaired spin densities. The unpaired spin density in an allyl radical is $+\,^{2}/_{3}$ at each of the two terminal carbon atoms and is $-^{1}/_{3}$ at the middle carbon atom.[5] Consequently, it is reasonable to visualize that the Pd in I is situated off center and is closer to the terminal carbon atoms as shown in the perspective figure above.

The non-classical structure of II eliminates the possibility of geometrical isomerism. Spin-lattice relaxation time measurements[6] indicate that the cyclopendiene groups in ferrocene are freely rotating. We have looked carefully for geometric isomers of II and found none. The crude product obtained as a tan, methylene chloride-soluble solid in 96.5% yield, was chromatographed analytically on alumina. Elution with methylene chloride–acetonitrile (65 fractions) gave an 88.6% yield of II. The n.m.r. spectra of the first and last fractions were identical.

The non-classical structures proposed for the organometal part in I and II are further supported by infrared spectra.[7] The C–H stretching region in the spectrum of I has only three strong bands at 3012, 3053 and 3081 cm.$^{-1}$ with relative absorbance of 0.1, 0.22 and 0.27, respectively. These bands may be assigned to the $C\text{–}H_A$, $C\text{–}H_M$ and $C\text{-}H_X$ stretching modes. These three bands are present also in the spectrum of II together with the bands due to the methyl group. In II, the relative absorbance of the 3081-cm.$^{-1}$ peak decreased in magnitude and became comparable to the 3012-cm.$^{-1}$ peak.

It is realized that the structures proposed are tentative and that further evidence from X-ray study on single crystals is necessary.

Even though a hyperfine splitting of 0.2 c.p.s. can be detected easily, there is no measurable coupling between the M- and the X-protons. Karplus and Anderson[8] showed that it is the non-perfect-pairing valence-bond structures which contribute most to the contact coupling constants. The absence of coupling between the M- and the X-protons suggests that interference by the Pd d-orbitals may have reduced the contribution of the non-perfect-pairing structures to the ground state wave functions. Another possible explanation is that the HCH dihedral angle is 125°, in which case[9] the value of $J^{\mathrm{HH}}_{\mathrm{gem}}$ is zero. It is possible that both mechanisms contribute to the observed zero J_{MX} value.

The 60-mc. spectrum of allylcobalt tricarbonyl[10] is similar to that of I in all respects which suggests strongly the symmetrical non-classical structure for the allylcobalt portion of the molecule.

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(5) H. M. McConnell and D. B. Chestnut, *J. Chem. Phys.*, **27**, 984 (1957); H. M. McConnell, *ibid.*, **28**, 1188 (1958).

(6) C. H. Holm and J. A. Ibers, *ibid.*, **30**, 885 (1959).

(7) We are indebted to Mr. J. A. Gailey for the infrared determinations and interpretations; $CDCl_3$, $CHCl_3$ and CCl_4 were used as solvents.

(8) M. Karplus and D. H. Anderson, *J. Chem. Phys.*, **30**, 6 (1959); M. Karplus, *ibid.*, **30**, 11 (1959).

(9) H. S. Gutowsky, M. Karplus and D. M. Grant, *ibid.*, **31**, 1278 (1959).

(10) R. F. Heck and D. S. Breslow, THIS JOURNAL, **82**, 750 (1960).

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RECEIVED MAY 9, 1960

FACILE BROMINATION OF PYRIDINE-TYPE HETEROCYCLES AT THE β-POSITION[1]

Sir:

The extremely vigorous conditions required to effect (presumably electrophilic) substitution into the pyridine ring are well-known,[2] and substitution into a pyridine derivative already containing an electron-withdrawing group is virtually impossible, except in special cases. However, we have found that refluxing a solution of bromine (1.5 moles) and nicotinyl chloride hydrochloride (I)[3] (1 mole) in excess thionyl chloride (II) for 13–19 hr. produced, after hydrolysis, 70–75% yields of 5-bromonicotinic acid (III)[4] (purified m.p. 189–190°; lit. m.p.'s 183°[4] and 182–183°[5]), identified by conversion *via* the acid chloride (ammonia in chloroform) to 5-bromonicotinamide[6] [80% yield, m.p. 219–219.5° (from aqueous ethanol) calcd. for $C_6H_5N_2OBr$: C, 35.85; H, 2.51; N, 13.95. Found:[7] C, 36.15; H, 2.65; N, 13.66] and thence by a Hofmann reaction (sodium hypobromite) to the known 3-amino-5-bromopyridine (65–67% yield, m.p. 69–69.5°; lit. m.p.'s, 65°[8] and 66–67°[9]), whose diazonium salt was reduced[10] to the known 5-bromo-3-pyridylhydrazine, m.p. 111–115°, lit. m.p. 109–110°.[10]

Dropwise addition (cooling) of 50 ml. of II to 40 ml. of pyridine (IV) and then 65 ml. of bromine (during 2 hr. at 90°) and heating the resulting solution at 88–91° for 5 hr. afforded, after removal of excess bromine and II, steam distillation of the basified residue, and vacuum sublimation, 20–28% of almost analytically pure 3,5-dibromopyridine (V), m.p. 111–112° (lit. m.p.'s 110–111°[11] and 110°[12]), identical (mixed m.p. and infrared spectrum) with

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(1) (a) Taken, in part, from the doctoral dissertation of C. V. Greco. (b) Supported, in part, by a research grant (CY-2962) from the National Cancer Institute of the Public Health Service and by the U.S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 18-(603)-127. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) For a recent review, see K. Thomas and D. Jerchel, *Angew. Chem.*, **70**, 719 (1958).

(3) A. L. Mndzhoyan, *J. Gen. Chem.* (*U.S.S.R.*), **16**, 1029 (1946); *C.A.* **41**, 2737 (1947).

(4) G. B. Bachman and D. D. Micucci [THIS JOURNAL, **70**, 2381 (1948)] prepared III in 87% yield by heating I with bromine for 10 hr. at 150–170° and then hydrolyzing.

(5) H. Gilman and S. M. Spatz, *J. Org. Chem.*, **16**, 1485 (1951).

(6) Also prepared in 50–65% yield (based on nicotinic acid) by direct reaction of the bromination product from I with ammonia in chloroform.

(7) Combustion analyses by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

(8) H. J. den Hertog and J. P. Wibaut, *Rec. trav. chim.*, **55**, 122 (1936).

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(10) C. Zwart and J. P. Wibaut, *ibid.*, **74**, 1062 (1955).

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