Fluxional Sigmatropic Rearrangements. A Case for **Orbital Symmetry Control in** Triphenyl-7-cyclohepta-1,3,5-trienyltin¹

Sir:

The facile migration of allylic silyl or germyl groups on cyclopentadienes or indenes, it has been proposed,² as examples of [1,5] sigmatropic shifts, might allow an adequate test of chemical predictions from orbital symmetry considerations.³ This proposal is deficient at least to the extent that the postulated course of reaction



in these and other systems^{2,4} is identical with a 1,2 shift, the least-motion path. I now wish to report that in a new fluxional system, triphenyl-7-cyclohepta-1,3,5-trienyltin (3), migration of the triphenyltin occurs in a manner inconsistent with least motion behavior, to the furthest carbon away.

Addition of triphenylstannyllithium ($\geq 0.4 M$ in tetrahydrofuran)⁵ to cycloheptatrienylium fluoroborate under argon at ambient temperature affords a mixture of at least five components containing triphenyl-7cyclohepta-1,3,5-trienyltin (3) in about 40% of theory, along with dicycloheptatrienyl (58 \pm 1%), cycloheptatriene (1.4 \pm 0.1%) (both yields by glpc), and hexaphenylditin. The last products found in the mixture

 $R^-Li^+ + C_2H_2BF_4 \longrightarrow Li^+BF_4^- + (C_2H_2)_2 +$

$$\mathbf{R}_{2} + \mathbf{C}_{7}\mathbf{H}_{8} + \underbrace{\overset{H}{\overset{7}{_{5}}}_{\overset{1}{_{5}}}^{\mathbf{R}}}_{\mathbf{R}_{2}}^{\mathbf{R}} + \underbrace{\overset{H}{\overset{7}{_{5}}}_{\overset{1}{_{5}}}^{\mathbf{R}}}_{\mathbf{R}_{3}}^{\mathbf{R}} = \operatorname{GePh}_{3}$$

$$\mathbf{1}, \mathbf{R} = \operatorname{GePh}_{3}$$

$$\mathbf{2}, \mathbf{R} = \operatorname{SiPh}_{3}$$

$$\mathbf{3}, \mathbf{R} = \operatorname{SnPh}_{3}$$

correspond to self-couplings of triphenyltin and of cycloheptatrienyl,⁶ which could result from an electron transfer from the anions7 to the cation. Further discussion of this and the related syntheses of triphenyl-7cyclohepta-1,3,5-trienylsilane (2) and triphenyl-7-cyclohepta-1,3,5-trienylgermane (1) is deferred. Separation of this mixture by preparative dry column chromatography⁸ gives the tin compound as a yellow solid (mp 123° from hexane),⁹ isolated in 14% yield. All spectral data (mass spectra, ir, uv) are in accord with the

(1) Presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Abstract ORGN 126.

(2) R. B. Larrabee and B. F. Dowden, 158th National Meeting of the American Chemical Society, New York, N.Y., Sept 1969, Abstract ORGN 48; R. B. Larrabee and B. F. Dowden, Tetrahedron Lett., 915 (1970); A. J. Ashe, III, J. Amer. Chem. Soc., 92, 1233 (1970); Tetrahedron Lett., 2105 (1970).

(3) R. Hoffmann and R. B. Woodward, Science, 167, 825 (1970), and references therein; A. G. Anastassiou, Chem. Commun., 15 (1968). (4) A. Davison and P. E. Rakita, J. Organometal. Chem., 21, P55

(1970); F. A. Cotton and T. J. Marks, J. Amer. Chem. Soc., 91, 7523
(1969); F. A. Cotton, Accounts Chem. Res., 1, 257 (1968).
(5) C. Tamborski, et al., J. Org. Chem., 27, 619 (1962); H. Gilman,

et al., ibid., 27, 4232 (1962). (6) Cf. M. L. Morrell and G. Vincow, J. Amer. Chem. Soc., 91, 6389

(1969). (7) R. E. Dessy, W. Kitching, and T. Chivers, ibid., 88, 453 (1966), and subsequent papers.

(8) B. Loev and M. M. Goodman, Chem. Ind. (London), 2026 (1967). (9) Satisfactory elemental analyses were obtained for compounds 2 and 3.

proposed structure¹⁰ and are not remarkable, except for the proton magnetic resonance (pmr).

Triphenyl-7-cyclohepta-1,3,5-trienyltin (3) displays fluxional behavior, as indicated by the temperature dependence between 0° and at least 139°, of the pmr line shape. Coalescence¹¹ of the nonaromatic resonances of 3 (0.12 M in C_2Cl_4 under CF_4 with hexamethyldisiloxane as internal lock) to a single line near the numberweighted shift occurs well below 100° due to exchange among all of the protons on the seven-membered ring. The apparent activation energy (E_A) for exchange, from correlation of the full line width at half-height (δv) with temperature (Figure 1), is 10.1 ± 0.8 kcal mol^{-1.12} As application of this approximation (ln δv vs. T^{-1}) to earlier bullvalene data¹³ gives an activation energy in excellent agreement with that from complete line-shape analysis, it may be assumed that the systematic error of the approximation in this rate range is small. The line shape is insensitive, within experimental error, to an eightfold dilution, and also, below 40°, to an increase of solvent polarity (use of CD₃CN). From these data and the fact that H migration is relatively slow (see below), it is concluded that the triphenyltin group shifts in a rapid nonionic intramolecular fashion from carbon to carbon about the seven-membered ring.

That this shift is concerted (the prime consideration in any designed test of orbital symmetry predictions) follows from energy considerations. The dissociation energy (D_e) of a fluxional bond can be equated with the activation energy of a postulated two-step or noncon-

$$C_{7}H_{7} \longrightarrow C_{7}H_{7} + R \longrightarrow R \longrightarrow C_{7}H_{7}$$

$$E_{A}$$

$$E_{a} = D_{e}: \text{ nonconcerted}$$

$$E_{a} \leq D_{e}: \text{ concerted}$$

certed rearrangement. A sigmatropic reaction is concerted if its activation energy (E_A) or onset energy¹⁴ is significantly less than D_e . Obviously this criterion is free from the drawbacks encountered in comparison of observed behavior with that merely projected for putative nonconcerted pathways.

On heating as a melt under vacuum at 160°, 3 slowly converts to a mixture of at least four products including dicycloheptatrienyl, hexaphenylditin, and a nonfluxional isomer tentatively assigned the structure triphenyl-3-cyclohepta-1,3,5-trienyltin (4) from its pmr spectrum.



Most probably two independent parallel reactions

(10) The possibility that the structure of 3 is other than σ bonded J. E. Weidenborner and A. L. Bednowitz, IBM, Yorktown Heights, N. Y.

(11) Recent reviews: C. S. Johnson, Jr., Advan. Magn. Resonance, 1, 33 (1967); G. Binsch, Top. Stereochem., 3, 97 (1967).

(12) The range represents 95 % confidence limits.

(13) (a) M. Saunders, Tetrahedron Lett., 1699 (1963); (b) A. Allerhand and H. S. Gutowski, J. Amer. Chem. Soc., 87, 4092 (1965); (c) A. Allerhand, H. S. Gutowski, J. Jonas, and R. A. Meinzer, ibid., 88, 3185 (1966).

(14) M. Menzinger and R. Wolfgang, Angew. Chem., Int. Ed. Engl., 9, 438 (1969).

Journal of the American Chemical Society | 93:6 | March 24, 1971

occur: a proton shift giving the isomer, ¹⁵ and thermal cleavage of a relatively weak tin-carbon bond, followed by rapid self-dimerization.⁶ The initial rate (<3% conversion) of reaction of triphenyl-7-cyclohepta-1,3,5-trienyltin to dicycloheptatrienyl as a melt or in tetra-chloroethylene was determined at several temperatures and observed, in solvent, to be first order (Table I).

 Table I. Rate of Conversion of

 Triphenyl-7-cyclohepta-1,3,5-trienyltin to Dicycloheptatrienyl

Temp, °C	Initial concn, $M imes 10^2$	Rate, sec ⁻¹ \times 10 ⁶
	In tetrachloroethylene	
122	7.3	6
130	4.2	12
	7.7	11
140	3.0	32
	4.1	32
	7.0	34
	7.1	27
	Neat	
123		0.17
130		1.4
132		0.92
140	<u>. </u>	5.3

From the temperature dependence of the rate the activation energy in solvent is estimated as >25 kcal mol⁻¹.¹⁶ As the dissociation energy of the cycloheptatrienyl-tin bond is approximated by the activation energy for decomposition, and, as this is much greater than the activation energy for the tin migration, this fluxional rearrangement is most likely concerted and the predictions of orbital symmetry, if valid, should be fulfilled.

The first-order prediction from orbital symmetry (*i.e.*, on assumption of a suprafacial migration of triphenyltin, of retention of configuration at tin, and of nonparticipation of d orbitals in the transition state) for a concerted process is migration from C-7 to C-4, as an example of a sigmatropic rearrangement of the order



[1,5].³ This is indeed the predominant mode of triphenyltin migration, at least below 30°. At -19° , **3** (0.7 *M*, in CHCl₃-*d* + TMS as internal lock) has an allylic proton resonance (\equiv H₇ t, τ 6.38; $J_{7,1=6} \cong$ 4 Hz; $J_{7,Sn} = 68 \pm 2$ Hz; 0.9 H) and three partially resolved olefinic proton resonances (τ 3.5, 15.5 H). Relative to that observed for **1** and **2** (τ 7.80; 8.25) the H₇



Figure 1. Temperature dependence of pmr line width of coalesced cycloheptatrienyl resonances of triphenyl-7-cyclohepta-1,3,5-trienyltin at 60 MHz.

resonance is shifted to abnormally low field. The pattern of strong couplings between nonidentical adjacent 7-ring protons, with the exception of the weakly coupled $H_{3=4}$ resonance, as determined by double resonance (at -40°) allowed assignment of τ 4.9, 5.2, and 5.5 resonances mainly to $H_{3=4}$, $H_{2=5}$, and $H_{1=6}$, respectively.¹⁷

Saturation of the H₇ resonance at -10° causes an intensity decrease of the $H_{3=4}$ resonance. Thus chemical exchange due to triphenyltin migration occurs faster than proton relaxation¹⁸ at this temperature, and occurs in the direction $C_7 \rightarrow C_3$ in accord with the simple symmetry prediction. At higher temperatures both the $H_{3=4}$ and the $H_{1=6}$ resonances suffer an intensity decrease in the above Forsen-Hoffmann experiment-a result of a more rapid sequence of two productive exchanges. A further confirmation is the 60-MHz spectrum at 30° in which the $H_{2=5}$ resonance is significantly less broadened relative to the other 7-ring protons, a consequence of the fact that these nuclei exchange at but one-half the rate of the other protons by the proposed pathway. Therefore, in this temperature range at least, a symmetrical π -bonded (heptahapto) intermediate or transition state 5 is unimportant in this conversion. The facile migration of tin occurs not in a least-motion fashion, but in the direction predicted by symmetry—to the furthest carbon atom away.

It should be noted that evidence presented here for the direction of the migration pathway provides little evidence concerning mechanistic details, including the possible involvement of intermediates such as *endo*triphenyl-7-bicyclo[4.1.0]hepta-2,4-dienyltin (6). The



inferences concerning concertedness remain unchanged. To complete a test of orbital symmetry predictions requires demonstration of the following: the role, if any, of virtual atomic orbitals on tin and the stereochemistry of the migrating group.

Acknowledgments. Technical assistance of Miss Y. Y. Cheng is gratefully acknowledged. Determina-

⁽¹⁵⁾ Cf. H. Kloosterziel and A. P. ter Borg, Recl. Trav. Chim. Pays-Bas, 84, 245 (1965); R. W. Murray and M. L. Kaplan, J. Amer. Chem. Soc., 88, 3527 (1966).

⁽¹⁶⁾ This compares well with an estimate of 25 kcal mol⁻¹ from the difference of the tin-carbon bond energy of 47 kcal mol⁻¹ for the empirical stabilization energy for cycloheptatrienyl:^{16b}
(a) H. A. Skinner, Advan. Organometal. Chem., 2, 49 (1964); E. A. V. Ebsworth, "Organometallic Compounds of the Group IV Elements," A. G. MacDiarmid, Ed., Vol. I, Marcel Dekker, New York, N. Y., 1968, p 1; (b) G. Vincow and H. J. Dauben, Jr., J. Amer. Chem. Soc., 87, 3527 (1965).

⁽¹⁷⁾ Cf. H. Kessler and E. Müller, Z. Naturforsch. B, 22, 283 (1967); J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, J. Amer. Chem. Soc., 87, 3896 (1965).

⁽¹⁸⁾ Reviewed in R. A. Hoffman and S. Forsen, Advan. Nucl. Magn. Resonance, 1, 15 (1966).

tion of 100-MHz nmr spectra with T. Luisebrink and T. Hirakawa, IBM Research, San Jose, Calif., with D. Falcon, IBM, East Fishkill, N. Y., and disclosure of their results by A. J. Ashe (University of Michigan) and A. Davison (MIT) prior to publication are noted with great appreciation.

R. B. Larrabee

IBM T. J. Watson Research Center Yorktown Heights, New York 10598 Received October 15, 1970

On the Structures of the Oxo- and Hydroxo-Bridged, Binuclear Chromium(III)-Ammine Complexes. The Rhodo and Erythro Series¹

Sir:

Since their discovery in 1882 by Jorgensen,² the rhodo and erythro series of binuclear ammine complexes of chromium(III) have provided many challenges with regard to the elucidation of their exact constitution, their unusual acid-base isomerization behavior, their reaction kinetics, ³⁻⁹ and, more recently, their electronic structures and magnetic properties.¹⁰⁻¹⁴ By now it is well established that these complexes have as a common structural feature a single oxygen bridge, and undergo the following chemical transformations.



To date, evidence for these structural formulations has been mainly chemical and spectroscopic.³⁻¹⁴ X-Ray structural information on these complexes would be useful in confirming their presumed gross molecular structures (*i.e.*, angular about the bridge oxygen in the hydroxo-bridged species and linear in the oxo-bridged species), and in providing detailed bond distance information. The latter should aid in the interpretation of certain features of the magnetic and spectral properties of the complexes which are attributed to

(1) The terminology rhodo and erythro is taken here to refer to the classification of the binuclear chromium(III)-ammine complexes on the basis of the NH3 ligand-to-Cr atom ratio. For the rhodo series this is 10:2, and for the erythro series 9:2

(2) S. M. Jorgensen, J. Prakt. Chem., 25, 231, 398 (1882).

(3) K. A. Jensen, Z. Anorg. Allg. Chem., 232, 257 (1937).

(4) W. K. Wilmarth, H. Graff, and S. T. Gustin, J. Amer. Chem. Soc., 78, 2683 (1956).

(5) M. Linhard and M. Weigel, Z. Anorg. Allg. Chem., 299, 15 (1959). (6) G. Schwarzenbach and B. Magyar, Helv. Chim. Acta, 45, 1425 (1962).

(7) D. J. Hewkin and W. P. Griffith, J. Chem. Soc. A, 472 (1966).

(8) D. W. Hoppenjans, J. B. Hunt, and L. Penzhorn, Inorg. Chem., 7, 1467 (1968).

(9) D. W. Hoppenjans and J. B. Hunt, ibid., 8, 505 (1969).

(10) C. E. Schaffer, J. Inorg. Nucl. Chem., 8, 149 (1958).

(11) H. Kobayashi, T. Haseda, and E. Kanda, J. Phys. Soc. Jap., 15, 1646 (1960).

(12) A. Earnshaw and J. Lewis, J. Chem. Soc., 397 (1961).
(13) B. Jezowska-Trzbiatowska and W. Wojciechowski in "Theory and Structure of Complex Compounds," Macmillan, New York, N. Y.,

1964, pp 375-379 (14) L. Dubicki and R. L. Martin, Aust. J. Chem., 23, 215 (1970).

the exchange interaction between the two, spin $\frac{3}{2}$, Cr(III) ions in the dimeric unit.¹⁰⁻¹⁴ An X-ray study could also settle the geometric configuration of the tetraammine unit in the erythro series, which is still in doubt, since both cis and trans isomers are claimed to exist.9

The salts of these binuclear complexes have proven difficult to work with crystallographically because of their light and X-ray sensitivity, their unusual hydration problems, and their tendency to form twinned and disordered crystals. Recently, however, we have obtained fairly stable, single crystals of the basic rhodo chloride salt μ -oxo-bis[pentaamminechromium-(III)] chloride monohydrate and of the acid erythro chloride salt pentaamminechromium(III)-µ-hydroxoaquotetraamminechromium(III) chloride monohydrate, and wish to report our structural findings.

In the conversion of the acid rhodo chromium chloride salt $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5$ to the corresponding erythro series by the addition of base (see above diagram), the solution always goes through a deep blue intermediate color. This intermediate color is presumed to be due to the presence of the oxybridged species, [(NH₃)₅Cr(O)Cr(NH₃)₅]⁴⁺, which has been most frequently isolated as an unstable perchlorate salt.⁵ We have found that if this transformation is effected by dissolving the acid rhodo chloride in cold (5°) 2 N NH₄OH, shortly after dissolution there is a deposition of a quantity of the blue intermediate as a chloride salt. This precipitate can be filtered, washed with alcohol and ether, and air-dried. Examination under a polarizing microscope showed the residue to be composed of well-formed (if small) crystal plates which extinguish along face diagonals and exhibit some dichroism. The crystals were allowed to remain in air for several days and appeared to be quite stable in low humidity. Analytical data and the infrared spectrum⁶ for the compound confirmed its formulation as the oxo-bridged salt, $[Cr_2O(NH_3)_{10}]Cl_4 \cdot H_2O$.

A crystal of dimensions $0.08 \times 0.10 \times 0.14$ mm was mounted on a quartz fiber and precession photographs showed the compound to crystallize in the orthorhombic system. The absences h0l for l odd, 0kl for k odd, and hk0 for h odd uniquely identified the space group as D_{2h}^{15} -Pbca (no. 61). Unit cell dimensions from a least-squares refinement of 2θ angles of eight reflections are a = 11.65 (1), b = 13.67 (1), and c = 13.6712.08 (2) Å. An experimental density of 1.553 g cm^{-3} (by floatation in a CCl₄-*n*-hexane mixture) agrees with a calculated value of 1.554 g cm⁻³ based upon four formula units per cell. Since the general positions of this space group are eightfold, the dimeric cation is required to possess a center of symmetry in the crystal.

A total of 1085 independent reflections up to 2θ = 106° were collected by the θ -2 θ scan technique on a Syntex computer-controlled diffractometer, using Nifiltered Cu K $\bar{\alpha}$ radiation (λ 1.5418 Å). Of these, 547 having $I \ge 3\sigma(I)$ were corrected for Lorentz and polarization effects and for a slight falloff in intensity during data collection, and were used in the structure solution. The chromium atoms were readily located from a Patterson map and the remaining atoms by successive difference Fourier maps. The structure has been refined by the least-squares method employing anisotropic thermal parameters for all atoms and in-