

photoproduct and $\text{Cr}(\text{CN})_6^{3-}$ would have to exhibit almost identical emission spectra. For the foregoing reasons, we believe that all of the lifetimes arise from $\text{Cr}(\text{CN})_6^{3-}$.

The multiple lifetimes in the same solvent clearly point to the existence of more than one species with interconversion times exceeding the ${}^2\text{E}$ lifetime. A slow equilibrium between conformers⁴ can be ruled out by the time scale, $>0.1 \mu\text{s}$. However, exchange rates between hydrogen bonded solvent molecules and bulk solvent as small as $\sim 10^5 \text{ s}^{-1}$ have been found in amine-alcohol complexes.⁵ Water is an efficient quencher of $\text{Cr}(\text{CN})_6^{3-}$ luminescence, $\tau = 6.5 \text{ ms}$ in DMF,⁶ suggesting a strong solute-solvent interaction in aqueous media and the slow solvent exchange time is not too surprising.

The different wavelength dependence of τ in the two solvents warrants comment. Since water is a quencher, the longer lifetime in 80% glycerol-water is to be expected. If long wavelength excitation in the mixed solvent selects solvates with higher proportions of water in the solvation sphere, the lifetime should approach that found in aqueous solution. It is possible that at even longer wavelengths the lifetimes would be the same in the two solvents.

It is of interest to compare the behavior of $\text{Cr}(\text{en})_3^{3+}$ and $\text{Cr}(\text{CN})_6^{3-}$. In spite of the hydrogen bonding propensities of amines, water is a weaker quencher of the $\text{Cr}(\text{en})_3^{3+}$ emission, $\tau = 1.59 \mu\text{s}$ in H_2O and $2.26 \mu\text{s}$ in a glycerol-water solution of approximately 50 mol %. Furthermore, τ is the same with 460- and 520-nm excitation, although the latter wavelength is well past the absorption maximum. The solvent exchange rate for water-amine hydrogen bonds exceeds 10^9 s^{-1} ⁵ and multiple lifetimes are therefore not anticipated.

In order to underscore the relevance of the foregoing to photochemistry, it is useful to distinguish three classes of relaxation processes: (i) intramolecular, where the solvent sphere is unchanged; (ii) solvent, characterized by translation and rotation times of the bulk solvent; and (iii) solvate. Intramolecular relaxation times, e.g., vibrational relaxation, are $>10^{11} \text{ s}^{-1}$ while solvent relaxation times vary with viscosity but typically range from 10^8 to 10^{11} s^{-1} . Adamson has discussed the pertinence of solvent relaxation in the photochemical context.⁷ The distinction between solvent and solvate relaxation is not sharp, but solvate relaxation designates processes that are strongly dependent upon both solute and solvent. It should be emphasized that solvates are not exciplexes, which are stable only in excited states.

Much, if not all, $\text{Cr}(\text{III})$ photochemistry originates in the ${}^4\text{T}_2$ state. While the lifetimes of the solvent relaxed ${}^4\text{T}_2$ are not known, they are likely to be shorter than ${}^2\text{E}$ lifetimes. If solvate relaxation is slow enough to lead to multiple ${}^2\text{E}$ lifetimes, multiple solvates should also prevail on the time scale appropriate to ${}^4\text{T}_2$ reactions. It is then possible that photochemical and photophysical measurements do not pertain to the same species. Also, comparison of direct and photosensitized processes may be misleading if one solvate is preferentially excited or is a more efficient acceptor in energy transfer. The absence of multiple ${}^2\text{E}$ lifetimes does not, however, preclude multiple solvates in ${}^4\text{T}_2$ for photoreactions that take place promptly in ${}^4\text{T}_2$ without passing through ${}^2\text{E}$. The results of Kane-Maguire et al.⁸ may refer to a single species, but one cannot be certain.

It would be surprising if $\text{Cr}(\text{CN})_6^{3-}$ were the only metal complex with long-lived solvates. However, $\text{Cr}(\text{CN})_6^{3-}$ may be unique in having a τ with such a large environmental sensitivity.⁹ The most direct method to determine the effect, if any, of multiple solvates on photochemistry is to measure the photochemical yields as a function of exciting wavelength, including red-edge excitation.

Acknowledgments. This work was supported by the National Science Foundation (Grant MPS 74-18553).

References and Notes

- (1) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, London, 1970.
- (2) F. Castelli and L. S. Forster, *J. Am. Chem. Soc.*, **95**, 5395 (1973).
- (3) R. Krishnamurthy and W. B. Schaap, *Inorg. Chem.*, **2**, 605 (1963).
- (4) W. Liptay, H.-J. Schumann, and F. Petzke, *Chem. Phys. Lett.*, **39**, 427 (1976).
- (5) E. Grunwald, R. L. Lipnick, and E. K. Ralph, *J. Am. Chem. Soc.*, **91**, 4333 (1969).
- (6) H. Wasgestan, *J. Phys. Chem.*, **76**, 1947 (1972).
- (7) A. Adamson, *Adv. Chem. Ser.*, **No. 150**, 128 (1976).
- (8) N. A. P. Kane-Maguire, J. E. Phifer, and C. G. Toney, *Inorg. Chem.*, **15**, 593 (1976).
- (9) L. S. Forster, *Adv. Chem. Ser.*, **No. 150**, 172 (1976).

Claudio Conti, Leslie S. Forster*

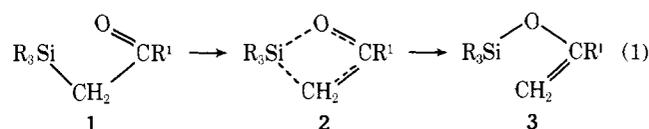
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

Received August 25, 1976

Reevaluation of Evidence Bearing on the Mechanism of the β -Ketosilane to Siloxyalkene Thermal Rearrangement

Sir:

Various accounts¹⁻⁴ of the course of thermal rearrangement of β -ketosilanes, **1**, to siloxyalkenes, **3**, present evidence purporting to be fully consistent with the intramolecular, four-center mechanism shown in eq 1. This claim is based essentially



on the following experimental facts: (a) When the carbonyl substituent R^1 in **1** varies in a series of para-substituted acetophenone derivatives, the Hammett $\rho = -0.78^3$ at 393 K; when one silicon substituent R in **1** is varied in a similar series of 1-(aryldimethylsilyl)-2-propanones, $\rho = +0.54^4$ at 433 K. (b) When **1** possesses a chiral silicon center, the configuration in the product of thermal rearrangement is completely retained. Though the possibility of a five-coordinate silicon intermediate involving d-orbital participation as well as pseudorotation has been considered² this was ruled out as inconsistent with the Hammett ρ constants^{3,4} which have been interpreted as an indication of almost no negative charge development on both the silicon and the carbonyl carbon. Moreover, molecular orbital calculations, stated³ to be in harmony with this interpretation, have been advanced to justify a sigmatropic rearrangement of silicon bridging the allylic framework with its d_{xz} and d_{yz} orbitals.

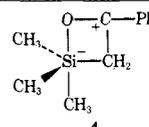
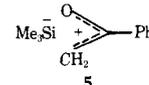
The analogous rearrangement of allylsilanes has been characterized⁵ as a fully concerted, orbital symmetry controlled migration of silicon involving a bridging 3_p orbital. The evidence for this conclusion is twofold: (i) the complete insensitivity of the experimental activation parameters to vari-

Table I. Effect of Solvent Composition on the Activation Parameters in the Rearrangement of Trimethylsilylacetophenone

Solvent composition	Medium dielectric ϵ	E_a (kcal)	Frequency factor A	ΔS^\ddagger (eu)
Benzene- d_6	2.28 ^a	30.6 ± 0.1	8.89×10^{13}	2.7 ± 0.3
Nitrobenzene-benzene- d_6 (4:1)	28.3 ^{a,b}	22.9 ± 0.8	1.25×10^{10}	-14.9 ± 2.0

^a CRC Handbook (20 °C). ^b Weighted average; nitrobenzene ($\epsilon = 34.8$) and benzene values.

Table II. Estimated and Experimental Calculations of the Isotope Effect for Silicon Migration in the Rearrangement of Trimethylsilylacetophenone at 397.75 K

Transition state Model		Part A. The Estimated Isotope Effects	Effective mass model	Estimated ^b k_L/k_H
 4		(45 + Si) — (14) Associative mechanism		1.003 ^a
 5		(45 + Si) --- (119) Dissociative mechanism		1.009 ^{a,c}
Part B. The Experimental Isotope Effects				
(²⁹ Si/ ²⁸ Si) ^c	<i>f</i> ^d	−ln(1 − <i>f</i>)	$\frac{[\ln(^{29}\text{Si}/^{28}\text{Si})_f]}{(^{29}\text{Si}/^{28}\text{Si})_0} (10^3)^e$	Exptl k_L/k_H
0.1789 ± 0.0004	0	0	0	—
0.1790 ± 0.0004	0.55	0.7985	5.588	1.0007 ± 0.0020
0.1785 ± 0.0005	0.65	1.0498	−2.238	0.9979 ± 0.0020
0.1799 ± 0.0004	0.75	1.3863	5.574	1.0040 ± 0.0020
0.1789 ± 0.0005	0.85	1.8971	0	1.0000 ± 0.0020
				1.0010 ± 0.0020

^a Reactant model = (45 + Si) — (119). ^b Estimated by using the Bigeleisen equation¹⁰ and the cutoff method.¹² Here k_L/k_H is the ratio $k_{^{28}\text{Si}}/k_{^{29}\text{Si}}$ of the two most abundant naturally occurring isotopes. ^c Determined isotope ratio in sample of residual reactant. ^d Fraction of reaction completed. ^e Natural logarithm of the isotope ratios at given extent of reaction "f" to original "o".

ation in the substitution of silicon and in the allyl side chain,⁵ and (ii) complete inversion of configuration in the rearrangement of a chiral silicon substrate.^{5b} These results are totally contrary to those reported¹⁻⁴ for the rearrangement **1** → **3**, where clearly the activation parameters³ are extremely sensitive to substitution; $\Delta E_a \approx 2$ kcal, and $\Delta(\Delta S^\ddagger) \approx 10.5$ eu for the change R = Ph to R = CH₃, and $\Delta E_a \approx 3.5$ –5.0 kcal, $\Delta(\Delta S^\ddagger) \approx 3$ –8 eu for the change R¹ = Ph to R¹ = CH₃. Moreover, the chiral results are exactly opposite; the β -ketosilane rearrangement proceeds with full retention^{1,2} and the sila-allylic with exclusive inversion.^{5b}

Some suspicion also focuses upon the interpretations of the Hammett ρ values,^{3,4} since the isokinetic temperature which can be calculated^{6a} from the reported data is about 380 ± 27 K, and the rate data bases for both sets of ρ values were gathered at temperatures very close to the isokinetic. Because ρ values will approach zero when the temperature of measurement is close to the isokinetic,^{6b} the actual magnitudes of ρ values measured at such temperatures tend to lose all mechanistic significance.

The argument against the fully concerted transition state **2** claimed for the β -ketosilane rearrangement, which up to now rests upon the comparison with the sila-allylic discussed above, is strongly supported by evidence gained through solvent effect studies. The classical picture of a reaction involving development of a charge separated state from neutral molecules, which requires a significant decrease in E_a and a more negative ΔS^\ddagger with more efficient solvation of the charge centers, is now well established.⁷ Thus, the finding (Table I) that in the rearrangement of **5** a solvent change from benzene to nitrobenzene produces $\Delta E_a = -7.7$ kcal and $\Delta(\Delta S^\ddagger) = -17.7$ eu is the clearest indication that a fully concerted transition state **2** does not prevail. By the same token this conclusive result also eliminates any possible radical dissociation–recombination mechanism and demands a polar course of rearrangement.

Faced with the problem of distinguishing between the two⁸ most probable polar mechanisms deducible from the above considerations, the heavy atom isotope criterion has been applied⁹ as a basis for decision between the following alternatives: (a) An *Associative Mechanism* requires a zwitterionic reaction intermediate like **4** (Table II) arising from octet expansion of the silicon. (b) A *Dissociative Mechanism* suggests that a

considerable degree of ionization of the silicon–carbon bond has created an ion pair intermediate like **5** (Table II).

Following the established procedures,^{9,11,12} the isotope effect k_L/k_H for the respective transition state models have been estimated and listed in Table II. While such values deduced with the aid of the simplifying assumptions of the cutoff method¹² are not exact, they do distinguish between the associative and dissociative mechanisms under consideration. A more exact treatment for the associative case would result in a lower value than $k_L/k_H = 1.003$ calculated by the cutoff method; the listed (Table II) value is therefore a *maximum*.^{9b} On the other hand, a more complete analysis would yield values of k_L/k_H for the dissociative mechanism which are higher than that listed in Table II. The $k_L/k_H = 1.009$ calculated by the simplified approach which neglects bonding other than along the reaction coordinate represents a *minimum*^{9c} value for the dissociative mechanism.

The actual silicon isotope effects in the β -ketosilane rearrangement were measured by the high-precision mass spectrometric procedures previously described.⁹ The Bigeleisen competitive method¹⁰ was applied in a form which permitted ready calculation of k_L/k_H from the isotope ratio determined at a known extent of reaction by means of these mass spectral procedures.

The experimental values of k_L/k_H (Table II) were mostly below the maximum value calculated for the associative mechanism, and completely out of range of the minimum value calculated for the dissociative mechanism. Taken in conjunction with the solvent effects observed on reaction rate (Table I), these data (Table II) establish beyond reasonable doubt that a trigonal bipyramid or the equivalent tetragonal pyramid¹³ structured intermediate is being formed in the course of the rate determining step of the rearrangement.

Thus, under these very favorable circumstances where a high energy Si–O bond is being created, the central silicon is enabled to undergo octet expansion with formation of five-coordinate structure. A similar pathway has been characterized⁹ for sulfur in the thioallylic rearrangement. The concerted, sigmatropic process identified in the analogous sila-allylic rearrangement⁵ is abjured only when an axial bond to a highly electronegative oxygen is possible to stabilize the trigonal bipyramid, thereby greatly lowering the activation requirement for the β -ketosilane

rearrangement. Moreover, contrary to the claim³ that "oxygen bond formation cannot significantly precede silicon-carbon bond breaking" based on the Hammett ρ value, it is now found that the Si-O bond formation is indeed the driving force of the reaction.

References and Notes

- (1) A. G. Brook, D. M. MacRae, and W. W. Limburg, *J. Am. Chem. Soc.*, **89**, 5493 (1967).
- (2) A. G. Brook, *Acc. Chem. Res.*, **7**, 77 (1974).
- (3) A. G. Brook, *J. Organomet. Chem.*, **86**, 185 (1975).
- (4) G. L. Larson and Y. V. Fernandez, *J. Organomet. Chem.*, **86**, 193 (1975).
- (5) (a) H. Kwart and J. Slutsky, *J. Am. Chem. Soc.*, **94**, 2515 (1972); (b) J. Slutsky and H. Kwart, *ibid.*, **95**, 8678 (1973).
- (6) (a) A plot from data provided in ref 4 of $\Delta H^\ddagger = \beta\Delta(\Delta S^\ddagger) + \Delta H_0^\ddagger$, the isokinetic relation, shows a slope $\beta = 381.9$ K and a correlation coefficient $r = 0.992$. (b) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).
- (7) H. Kwart and P. A. Silver, *J. Org. Chem.*, **40**, 3019 (1975).
- (8) If we neglect the Hammett ρ values^{3,4} as a mechanistic criterion because they have been determined at temperatures close to the isokinetic, there remain only two reasonable ways in which ionic or zwitterionic character can be developed in this reaction process.
- (9) (a) H. Kwart and J. Stanulonis, *J. Am. Chem. Soc.*, **98**, 4009 (1976). (b) An oxygen isotope effect correction was not made because this is a maximum value of the isotope effect. The reasoning is that a correction for the isotope effect of naturally abundant ¹⁸O (0.20%) would have resulted in a slightly lower magnitude. (c) A ¹³C isotope effect correction was not made because this is a minimum value of the isotope effect. The reasoning is that if a correction for bond breaking to naturally abundant ¹³C (1.1%) were made, the value calculated would be somewhat greater.
- (10) J. Bigeleisen and M. S. Mayer, *J. Chem. Phys.*, **15**, 261 (1947); J. Bigeleisen, *ibid.*, **17**, 675 (1949).
- (11) J. Bigeleisen in "Advances in Chemical Physics", I. Pregogine, Ed., Vol. 1, Interscience, New York, N.Y., 1958.
- (12) M. J. Stern and M. Wolfsberg, *J. Chem. Phys.*, **45**, 4105 (1966).
- (13) L. H. Sommer and D. L. Bauman, *J. Am. Chem. Soc.*, **91**, 7045 (1969).

H. Kwart,* W. E. Barnett

Department of Chemistry, University of Delaware
Newark, Delaware 19711

Received August 24, 1976

Structure and Magnetic Properties of a Unique Cobalt(II) Hippurate Complex: a Canted, Oxygen Bridged, Metamagnet

Sir:

Interest in the low temperature magnetic properties of multinuclear transition metal complexes has accelerated in the past few years as adequate experimental systems and theoretical models have been developed for data collection and interpretation.¹ Many examples of ferromagnetic and anti-ferromagnetic long-range ordering have been observed, particularly in carboxylate and halide complexes of the first-row transition metals.²⁻³ However, few magnetically ordered compounds have been characterized which exhibit metamagnetic phase transitions. Most of the reported cases of metamagnet behavior involve linear chain molecules with metal centers bridged by halides⁴⁻⁶ although the phenomenon has been observed in neptunium(V) oxalate, (NpO₂)₂C₂O₄·4H₂O.⁷ This communication reports the preparation and characterization of the first example of an apparent metamagnet which has water molecules bridging the metal centers.

A compound of empirical formula, Co[(C₆H₅)-CONHCH₂COO]₂·5H₂O, was prepared by adding 1.82 g of Co(ClO₄)₂·6H₂O in 20 ml of distilled water to 2.01 g of sodium hippurate (sodium *N*-benzoylglycinate) in 50 ml of distilled water. Pink needles began to form after 4-5 h. The product was filtered and recrystallized from a 1:1 water/ethanol mixture. The stoichiometry was established by elemental analysis with the number of water molecules verified from the initial weight loss in the thermal gravimetric curves obtained on a Perkin-Elmer differential scanning calorimeter DSC-1B (values were reproducible to $\pm 0.1\%$ H₂O).⁸

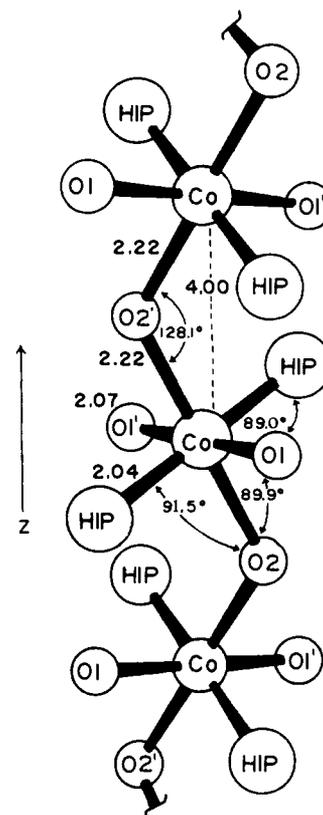


Figure 1: Projection view of the site symmetry about the Co(II) ions.

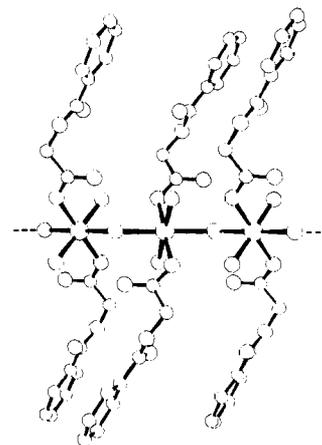


Figure 2: Projection view of the Co[(C₆H₅)CONHCH₂COO]₂·5H₂O molecule.

The compound crystallizes in the monoclinic space group *C2/c* with four formula weights in a unit cell of dimensions $a = 40.82$, $b = 6.90$, $c = 7.99 \pm 0.01$ Å and $\beta = 91.9 \pm 0.1^\circ$. Intensity data were collected out to a 2θ limit of 100° on a G.E. XRD-490 fully automated diffractometer system using Cu K α radiation. A total of 715 reflections were considered statistically significant and used in the subsequent refinement. At the present stage of refinement using anisotropic temperature factors and fixed hydrogens calculated from predicted geometry, the structure calculation has progressed to the point where the reliability index has a value of $R = 0.094$.⁹

The backbone of the structure, shown in Figure 1, is made up of cobalt ions linked in infinite chains along the z cell axis. Each cobalt is bonded to two hippurate molecules and two water molecules in the central plane. These planes are then connected by a water bridge having a longer bond than the other cobalt-oxygen distances, forming a tetragonally distorted octahedron.⁸ The closest cobalt-cobalt distance is 4.00 Å across