

both organic and metal-organic chromophores.¹¹ Moreover, when implemented within the framework of a sum-over-states perturbation theoretic description of microscopic polarizability,^{5-7,12} we recently showed ZINDO to reproduce accurately experimental organic π -electron β parameters ranging over 3 orders of magnitude.¹³ The present β_{ijk} calculations focused on several diverse types of transition-metal organometallic molecules for which solution-phase β_{vec} ¹⁴ values have been determined by using dc electric field induced second harmonic generation (EFISH) techniques.³ Metrical parameters were taken from relevant crystal structure data,^{2,15} and the basis set of configuration interaction states included 130 monoexcited states (at which point convergence was observed in all cases). Standard ZINDO transition-metal parameters^{9a,b,11} were employed,¹⁶ and the sum-over-states MECI (monoexcited configuration interaction) method was used to compute β_{ijk} .⁵⁻⁷

ZINDO-derived β_{vec} ¹⁴ and β_{tot} ¹⁷ values are compiled and compared to experimental data in Table I and Figure 1 for the three classes of organometallic chromophores. Considering experimental uncertainties and the wide diversity of complex molecular structures¹⁸ and substituents involved, as well as the large dispersion in the magnitudes and signs of β_{vec} , the overall agreement with experiment is generally good in terms of orderings, signs, and magnitudes. For molecules 1-7, we calculate that the ferrocenyl unit behaves as a simple π -donor substituent with β_{vec} in **2** dominated by a single charge-transfer state (MLCT + LLCT) involving the redistribution of 0.4 electrons from the ferrocenyl moiety to the nitro (acceptor) substituent. This transition is calculated to have an oscillator strength of 0.98, a dipole moment change ($\Delta\mu_{\text{ge}}$) of 11.0 D, and $\lambda_{\text{max}} = 378$ nm (observed $\lambda_{\text{max}} = 356$ nm in dioxane solution^{3a}). Metal d-d transitions contribute little to β_{vec} , and the dominant excitation direction closely parallels the dipole moment vector ($\beta_{\text{vec}} \approx \beta_{\text{tot}}$). Not surprisingly, substituents that enhance the ferrocenyl donor character (**4**, **5**) enhance β_{vec} . In sum, the electronic structural origin of the second-order nonlinearity in **1-7** closely parallels that of the analogous stilbene chromophores.^{5a,6c,19}

The ZINDO results for **8-12** reveal that the ground-state dipole moments are antiparallel to those in the excited states which dominate β_{vec} . This convincingly explains the observed negative signs of β_{vec} and arises here because pyridine functions as the strongest σ -donor ligand in the ground state and as the strongest π -acceptor in the relevant excited states. In a simple two-level picture,^{16,20} the modest β_{vec} values observed arise because the dominant states do not involve large $\Delta\mu_{\text{ge}}$ values, primarily because tungsten is effectively in an electronically pseudocentrosymmetric environment, surrounded by ligands having unfavorably similar donor/acceptor character. The calculations reveal an analogous situation for **13-18** with the effective electronic pseudocentrosymmetry again leading to undesirable, β -lowering competition between π -acceptors in the various contributing states.

These results indicate that a useful quantum chemical formalism is now available for understanding the quadratic NLO properties of known metal-organic chromophores as well as for aiding in the design of new ones. The richness of mechanisms operative in such chromophores includes both β_{vec} -enhancing charge-transfer processes across the length of the molecule as well as β_{vec} -limiting competition among π -acceptor ligands in coordination spheres having effective electronic centrosymmetry.

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Racemization and Geometrical Isomerization of (-)-(R,R)-Cyclopropane-1,2-²H₂

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Since the thermal interconversion of *cis*- and *trans*-cyclopropane-1,2-²H₂ was discovered more than 30 years ago,¹ theoretical and experimental studies have been attracted to different instances of this process.² Most of the sophisticated theoretical work has considered only cyclopropane and related trimethylene diradical species,³ while experimental efforts have been largely directed toward cyclopropanes substituted with various functional

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(14) For $i = x, y, \text{ or } z$,

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{j \neq i} (\beta_{jji} + \beta_{jii} + \beta_{ijj})$$

$$\beta_{\text{vec}}(-2\omega; \omega, \omega) = \sum_{i=1}^3 \frac{\mu_i \beta_i}{|\mu|}$$

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(16) Since tungsten ZINDO parameters are not yet available, calculations were performed on the molybdenum analogues, a reasonable approximation.³

(17) $\beta_{\text{tot}} = (\beta_1^2 + \beta_2^2 + \beta_3^2)^{1/2}$

(18) Molecular mechanics calculations indicate that the stilbene fragment of **6** is unlikely to be rigorously planar, as assumed in the β_{vec} calculation. This is expected to lower $\beta_{\text{vec}}^{\text{exp}}$, as observed.

(19) (a) Singer, K. D.; Sohn, J. E.; King, L. A.; Gordon, H. M.; Katz, H. E.; Dirk, C. W. *J. Opt. Soc. Am. B* **1989**, *6*, 1339-1351. (b) $\beta_{\text{vec}}^{\text{PPP}} = 73.3 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$ ($\hbar\omega = 0.656 \text{ eV}$) for the *p*-(N,N-dimethylamino)phenyl analogue of **2**.^{6c}

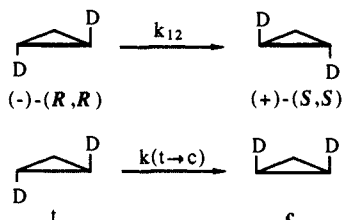
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groups.⁴ Otherwise unsubstituted isotopically labeled cyclopropanes offer the best prospects for bridging this significant discrepancy, but both synthetic and analytical difficulties have severely restricted experimental efforts in this area: there has been no kinetic work on the stereomutations of isotopically labeled cyclopropanes for more than 15 years, and early work was limited to just one set of isomers, the three 1,2-*d*₂-cyclopropanes.^{1,5-7}

In 1974, the rate constant for racemization of (+)-(*S,S*)-cyclopropane-1,2-²H₂ ($k_a = 2k_{12} + k(t \rightarrow c)$) was found to be only slightly slower than that for cis,trans isomerization ($k_1 = 2k(t \rightarrow c)$): $k_1/k_a = 1.07 \pm 0.04$ at 422.5 °C. This k_1/k_a ratio does not, unfortunately, measure the relative importance of one-center and two-center epimerizations, the mechanistically significant distinction, for there are only two experimentally accessible kinetic parameters and three unknowns, since $k(t \rightarrow c) = 2k_1$ (when C1-C2 breaks) + $2k$ (when C1-C3 or C2-C3 breaks).



One attempt to confront this limitation through making assumptions about secondary deuterium isotope effects led to the conclusion that these stereomutations occur predominantly, if not exclusively, through two-center epimerizations ($k_{12} \gg k_1$): "the theoretically predicted double rotation mechanism predominates."⁷ This striking conclusion, at odds with the experimentally demonstrated stereochemical pattern shown by every other substituted cyclopropane subjected to appropriate kinetic study (some dozen cases, $(k_1 + k_2) \geq k_{12}$),⁴ depends both on the accuracy of the measured k_1/k_a ratio and on the assumptions employed when this ratio is interpreted. The first of these factors has now been redetermined: we have reexamined the kinetics of isomerization of the 1,2-*d*₂-cyclopropanes, employing different synthetic methods to secure all three isomers and different analytical techniques to define the two experimentally accessible parameters.

The (+)-*S,S* and (-)-*R,R* trans isomers and racemic trans material were available from prior work;⁸ *cis*-cyclopropane-1,2-²H₂ was prepared⁹ from 3-(ethoxycarbonyl)cyclopropene through reduction with LiAlD₄ followed by a workup using D₂O;¹⁰ oxidation (PCC, then Ag₂O and NaOH) to give 2,3-*syn,cis*-cyclopropane-2-²H₂-carboxylic acid; LiAlH₄ reduction; PCC oxidation; and finally decarbonylation with ClRh(PPh₃)₃. The *d*₂-cyclopropanes were purified by gas chromatography and characterized by Fourier transform infrared spectroscopy (FTIR), tunable diode laser spectroscopy, and mass spectrometry.

At 422.5 °C in the gas phase, with pentane as a bath gas and total pressures of 640–700 Torr, the rate of approach to the *cis,trans* equilibrium was followed by using 1–10-mg samples of

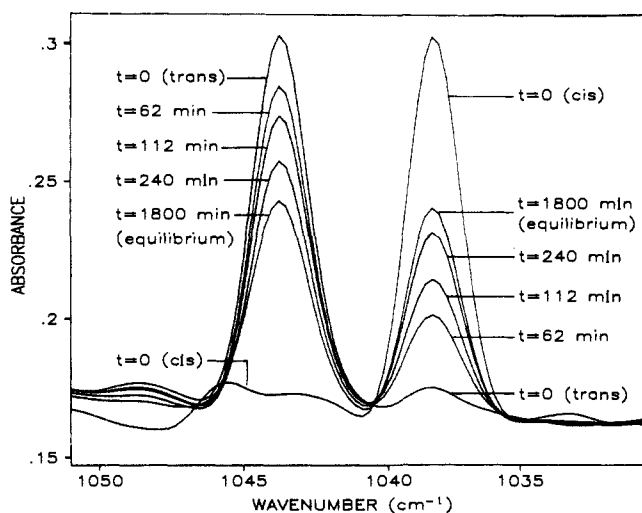


Figure 1. FTIR spectra of kinetic samples in the gas phase (4.5 mg for each sample) as a function of thermolysis reaction time. The absorbance band for *cis*-cyclopropane-1,2-²H₂ is at 1038.4 cm⁻¹, and the corresponding band for the *trans* isomer is at 1043.7 cm⁻¹.

Table I. Loss of Optical Activity for (-)-(*R,R*)-Cyclopropane-2-²H₂ at 422.5 °C Determined by VCD Spectroscopy

time, min	pressure, Torr			α_{rel}	
	sample	ref ^a	$ \Delta A/\Delta A_{ref} $	exptl ^b	calcd ^c
62	130.0	110.9	0.9275	0.791	0.797
112	138.0	106.6	0.7295	0.563	0.551
240	152.0	97.1	0.3209 ± 0.005^d	0.205 ± 0.003^d	0.214

^a The (+)-*S,S* reference sample was of 79.4% apparent optical purity. ^b Calculated from the equation $\alpha_{rel} = (\text{pressure(ref)}/\text{pressure(sample)}) \times |\Delta A/\Delta A_{ref}|$. ^c Calculated from the nonlinear least-squares-derived equation $\alpha_{rel} = 1.26 \exp(-12.3 \times 10^{-5} \text{ s}^{-1}t)$. ^d Duplicate determinations, separated by six months and one relocation of instrumentation to a new building.

labeled cyclopropane substrates. An equilibrium sample obtained by heating racemic *trans* starting material at 422.5 °C for 1800 min (over 21 half-lives) was taken to be a 1:1 *trans-cis* mixture. Three product mixtures from (-)-(*R,R*)-cyclopropane-1,2-²H₂ as well as starting material and the equilibrium mixture gave $k_1 = (13.3 \pm 0.22) \times 10^{-5} \text{ s}^{-1}$ (SD, three kinetic points)¹⁴ using gas-phase FTIR spectroscopy at 1035–1045 cm⁻¹ and the partial least squares program PLSQUANT in the SpectraCalc software package from Galactic Industries to analyze spectra (Figure 1). The samples were analyzed on a Nicolet 7199 FTIR instrument acquiring 2048 scans at 2-cm⁻¹ resolution using 4.5-mg samples in a 5-cm path length vacuum-tight cell equipped with cold finger and KBr windows. An independent determination of this rate constant using racemic *trans*, *cis* *trans*, and *cis* starting materials, tunable diode laser spectroscopy at 1028 cm⁻¹ as the analytical method,¹¹ and a nonlinear least-squares treatment of the data for nine reaction mixtures gave $k_1 = (13.6 \pm 0.26) \times 10^{-5} \text{ s}^{-1}$ (SD, nine kinetic points), in satisfactory agreement with the FTIR result. The weighted mean k_1 is $(13.4 \pm 0.17) \times 10^{-5} \text{ s}^{-1}$.

The kinetics of racemization were followed by vibrational circular dichroism (VCD) spectroscopy, a technique demonstrated to give accurate enantiomeric excess values for synthetic mixtures of the chiral *trans* and achiral *cis* isomers.¹² For each determination, four VCD spectra were obtained: a spectrum of unreacted (+)-*S,S*, one of racemic *trans*, one of the (-)-*R,R* kinetic sample, and one of racemic *trans* containing the same amount of achiral *cis* material as in the (-)-*R,R* kinetic sample. The VCD spectrum of the racemic *trans* sample was utilized as an instrumental base line relative to which the VCD spectrum of the unreacted (+)-*S,S*

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sample was referenced. In order to eliminate artifacts generated by the presence of *cis-d*₂-cyclopropane in kinetic samples, the VCD spectrum of the (-)-*R,R* kinetic sample was referenced against racemic trans containing the same amount of cis isomer present in a kinetic sample. VCD intensities of the resulting base-line-corrected spectra were measured in volts relative to the racemic base line for 90 data points between 2310 and 2290 cm⁻¹. The ratios of all 90 data points were averaged to obtain a measure of the ratio $|\Delta A/\Delta A_{ref}|$ for each kinetic sample (Table I). Four separate determinations of $|\Delta A/\Delta A_{ref}|$ were performed on successive days for each sample. A nonlinear least-squares treatment of the data for the chiral kinetic samples gave rate constant $k_\alpha = (12.3 \pm 0.65) \times 10^{-5} \text{ s}^{-1}$ (SD, three kinetic points).

With VCD spectroscopy, it was possible to use samples between 2 and 3 orders of magnitude smaller than those employed by Berson and Pedersen⁷ using optical polarimetry, thus greatly alleviating difficulties posed by synthetic and gas chromatographic problems of scale, and of expense. The promise of VCD spectroscopy for kinetic studies¹³ seems very bright indeed.

The present determinations of k_i and k_α are each about twice as large as the values reported earlier,⁷ which could easily be associated with small differences in temperature, pressure, or bath-gas effects; yet the ratio of rate constants now found, $k_i/k_\alpha = 1.09 \pm 0.05$, is in fine agreement with the report of Berson and Pedersen.⁷ The final resolution of the problem posed by the apparently dichotomous stereomutation propensities of deuterium-labeled cyclopropanes and other substituted cyclopropanes must await either new information relevant to the deuterium kinetic isotope effects that may be in play, or experiments with some new set of labeled isomers, providing as many experimentally measurable rate parameters as there are distinct rate constants for one-center and two-center epimerizations to be derived. One may even now, though, be more assured that the problem is not an illusion predicated on an inaccurate experimental value for k_i/k_α .

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Unprecedented, Bridged Dihydrogen Complex of a Cofacial Metalloporphyrin and Its Relevance to the Bimolecular Reductive Elimination of Hydrogen

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Recently, we characterized the first metalloporphyrin dihydrogen complex, Os(OEP)(H₂), and proposed that a similar ruthenium porphyrin dihydrogen complex, Ru(OEP)(H₂), is involved as an intermediate in the catalytic H/D isotopic exchange between water and hydrogen.^{2,3} We now report that treatment

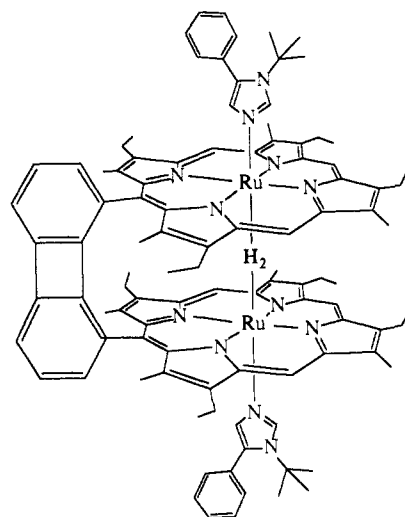


Figure 1.

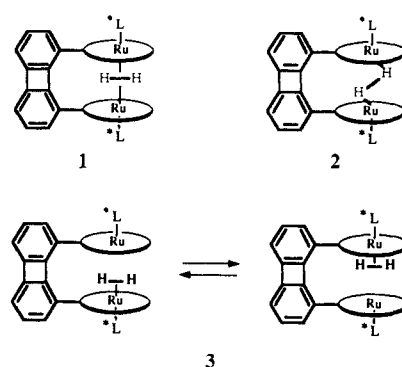


Figure 2.

of a metal-metal-bonded cofacial ruthenium porphyrin dimer with a sterically bulky ligand in the presence of hydrogen gas has yielded the first known complex containing a dihydrogen ligand bound between two metals. Such a bridged dihydrogen complex is proposed as an intermediate in the bimolecular elimination of dihydrogen from two metalloporphyrin hydrides.

Addition of 2 equiv of 1-*tert*-butyl-5-phenylimidazole, *L, to a hydrogen-saturated benzene solution of the cofacial metalloporphyrin dimer Ru₂(DPB)⁴ resulted in the immediate formation of Ru₂(DPB)(*L)₂(H₂),⁵ which displayed a broad singlet at $\delta = -38.6$ ppm in the ¹H NMR spectrum,⁶ indicating the presence of a metal-bound hydride or dihydrogen ligand.⁷ When the same reaction was performed with hydrogen deuteride (instead of hydrogen), the broad singlet was replaced by a 1:1:1 triplet at $\delta = -38.4$ ppm ($J_{HD} = 15 \pm 1$ Hz) while the rest of the ¹H NMR spectrum remained unchanged. Additionally, the minimum relaxation time of the metal-bound protons was 132 ± 6 ms as determined by variable-temperature ¹H NMR measurements (400 MHz, 20 °C, toluene-*d*₈).^{9,10} These values for J_{HD} and T_1 (min)

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(5) Under an argon atmosphere, a solution of Ru₂DPB in *d*₆-benzene (0.5 mL of a 1.38 mM stock solution) was bubbled for 5 min with hydrogen. Two equivalents of 1-*tert*-butyl-5-phenylimidazole (58 μ L of a 26.5 mM stock solution in *d*₆-benzene) was added, and hydrogen bubbling was continued for 2 min.

(6) ¹H NMR (C₆D₆, ppm): porphyrinic resonances, H_{meso} 8.81 (s, 2 H), 8.72 (s, 4 H); biphenylene 7.15 (2 H, obscured by residual solvent peak), 7.06 (d, 2 H), 6.85 (t, 2 H); CH₂CH₃ 4.38 (m, 8 H), 3.91 (m, 8 H); CH₃ 3.50 (s, 12 H), 3.25 (s, 12 H); CH₂CH₃ 1.81 (t, 12 H), 1.61 (t, 12 H); imidazole resonances, *p*-phenyl 6.21 (t, 2 H); *m*-phenyl 5.99 (t, 4 H); *o*-phenyl 4.38 (d, 4 H); H_{imidazole} -0.34 (s, 2 H), -0.40 (s, 2 H); *tert*-butyl -0.86 (s, 18 H). Ru-H₂ -38.6 (br s, 2 H). Ru-HD -38.4 (t, $J_{HD} = 15 \pm 1$ Hz).

(7) The hydride and dihydrogen ligand resonances of metalloporphyrins are shifted to very high field in the ¹H NMR spectra by the porphyrin ring current effect.^{3,8}

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(2) Abbreviations: OEP = octaethylporphyrinato dianion; DPB = diporphyrinatobiphenylene tetraanion; THF = tetrahydrofuran; PPh₃ = triphenylphosphine; FeCp₂ = ferrocene.

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