In conclusion, our results suggest that the chemistry of **7** and **12** in solution is the chemistry of "carbene complexes"[25] affording nearly exclusively **6**, while in the "gas phase" the typical products of **5** become dominant.[26] Carbenoid chemistry the alkyllithium way can be shifted toward chemistry expected from free carbenes with our new method. Thus, the geminal dibromides studied in the gas phase give higher yields of hydrocarbons—thought to stem from free carbenes—than in solution. In cases in which a tosylhydrazone cannot be synthesized, the decomposition of geminal dibromides may be an alternative to the Bamford–Stevens reaction. From the product ratios of vinylallene (**3**) and cyclopentadiene (**15**), $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ of the competing cyclopropylidene–allene and carbene–carbene rearrangement $\mathbf{1} \rightarrow \mathbf{2}$ can be determined.

Acknowledgment. We gratefully acknowledge support of this work by the Deutsche Forschungsgemeinschaft. We thank K. Gomann for skillful experimental and technical assistance.

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Carbon-13 Magnetic Resonance Dipolar Spectroscopy. Orientation of the Chemical Shift Tensor in Cyclopropane

Kurt W. Zilm,[†] Alvin J. Beeler, David M. Grant,[*] Josef Michl, Teh-Chang Chou, and Evan L. Allred[*]

Department of Chemistry, University of Utah Salt Lake City, Utah 84112 and the University of Utah Research Institute Salt Lake City, Utah 84112

Isotropic carbon-13 chemical shifts of methylenes in three-membered rings are well-known to be anomalously upfield (~ 20 ppm) from other aliphatic chemical shifts. Recently this laboratory reported the chemical shift tensor for the methylene in cyclopropene[1] (Table I), where it was found that the unusually high-field isotropic shift of 2.3 ppm from Me_4Si was a consequence of only one component (σ_{33}) appearing at a rather surprising high-field value of -59 ppm from Me_4Si. The other two components were found at typical aliphatic shielding values. We now find that cyclopropane also gives a similar result (Table I). To understand better these shielding phenomena, we undertook a study to determine the orientation of the shift tensor with respect to the molecular frame in cyclopropane. This is usually accomplished by analysis of spectral patterns[2] obtained from a single crystal in various orientations. The experimental difficulties associated with performing such an experiment on a small molecule like cyclopropane make this approach unappealing.

A ^{13}C cross-polarization (CP) spectrum of matrix-isolated cyclopropane containing a pair of adjacent carbon-13 nuclei will reflect the ^{13}C–^{13}C dipolar coupling.[3] As both the splitting produced by the dipolar interaction and the chemical shift depend on the molecular orientation relative to the magnetic field, the

[*] University of Utah.
[†] University of Utah Research Institute. All others at the University of Utah.

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(2) Pausak, S.; Pines, A.; Waugh, J. S. *J. Chem. Phys.* **1975**, *59*, 591.
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Table I. ^{13}C Shift Tensors for CH_2 in Cyclopropane and Cyclopropene[a]

	σ_{iso}(liq)	σ_{11}	σ_{22}	σ_{33}
cyclopropane	−3.8	22	2	−36
cyclopropene[b]	2.3	40	29	−59

[a] All shifts in ppm from external Me_4Si. Estimated errors ±2.5 ppm. [b] Reference 1.
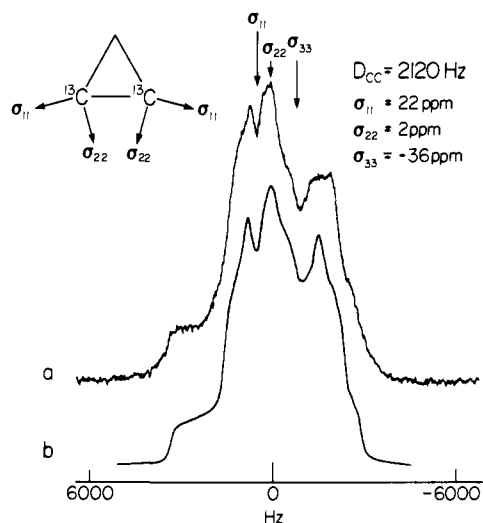
Figure 1. (a) Experimental ^{13}C spectrum taken at 20.12 MHz. (b) Simulation using the parameters in the inset. σ_{11} and σ_{22} are oriented on each carbon as shown. σ_{33} is perpendicular to the plane of the drawing. Note that when H_0 is along σ_{11} for one of the ^{13}C's, the other resonates at $^3/_4\sigma_{22} + ^1/_4\sigma_{11}$.

powder pattern produced will contain the information needed to relate the cyclopropane chemical shift tensor to the dipolar vector and thus the molecular frame.

Doubly ^{13}C-labeled cyclopropane for the matrix experiment was synthesized from diethyl malonate-*1,3-^{13}C* (Merck and Co. Inc., 90 atom % ^{13}C) as outlined in the sequence of reactions in (1). The ring-closure step was accomplished by a specially activated Zn–Cu reagent.[4]

$$H_2C \overset{^{13}CO_2Et}{\underset{^{13}CO_2Et}{<}} \xrightarrow[\text{2 } H_2O/NaOH]{\text{1 LiAlH}_4 \text{ Et}_2O} \xrightarrow[\text{90 °C/18 h}]{48\% \text{ HBr} \text{ H}_2SO_4} \xrightarrow[\substack{75\% \text{ EtOH-H}_2O \\ \text{reflux } 7 \text{ h}}]{\text{Zn-Cu} \text{ NaI/Na}_2CO_3} H_2C \overset{^{13}CH_2}{\underset{^{13}CH_2}{<}} \quad (1)$$
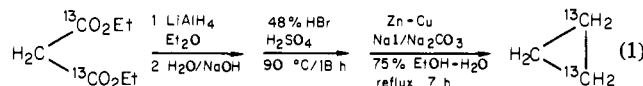
The principal axes of the ^{13}C chemical shift tensor are easily specified by the local C_{2v} symmetry at the carbon nucleus[5] if intermolecular effects are taken to be negligible. Two axes are constrained to be perpendicular to the two mirror planes and the remaining axis must lie along the C_2 axis (Figure 1). It should be noted that the two ^{13}C nuclei in cyclopropane do not constitute a simple A_2 spin system in the solid state as the nuclei do not have the same shift at all possible orientations of the field with respect to the molecule because all of the principal shielding axes are not coparallel. When the difference in these resonant frequencies ($\Delta\nu$) is comparable to the dipolar coupling, the spectrum becomes second order in the same sense as a typical AB system. For an AB dipolar coupled system the four transitions and concomitant transition probabilities for any one orientation are given by[3]

$$\nu_{a\pm}(\theta,\phi) = \frac{\nu_1 + \nu_2}{2} - \frac{A}{2} \pm C \qquad P_{a\pm}(\theta,\phi) = 1 \pm B/C$$

$$\nu_{b\pm}(\theta,\phi) = \frac{\nu_1 + \nu_2}{2} + \frac{A}{2} \pm C \qquad P_{b\pm}(\theta,\phi) = 1 \mp B/C$$

$$A = D(1 - 3\cos^2\theta) + J$$

(4) Hassner, A.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 2879.
(5) Buckingham, A. D.; Malm, S. *Mol. Phys.* **1971**, *22*, 1127.

$$B = \tfrac{3}{4}(J - A/3)$$

$$C = (\tfrac{1}{2}\Delta\nu + B)\sqrt{1 - [4B\Delta\nu/(\Delta\nu + 2B)^2]}$$

$$D = \gamma_1\gamma_2\hbar/r_{12}^3$$

$$\Delta\nu = \nu_1 - \nu_2$$

where these parameters are given in Hz with D and J as the direct and indirect dipolar coupling constants, respectively. Both ν_1 and ν_2 have the usual tensorial orientational dependence, J is the indirect dipolar coupling constant (assumed to be isotropic here), r_{12} is the internuclear distance, and θ is the angle between H_0 and the dipolar vector. The powder spectrum may be calculated from these formulas[3] in a straightforward fashion, giving a spectrum that is the sum of two modified Pake doublets.[6]

Within the constraints of symmetry there are six possible ways in which to assign the three shielding tensor elements to the principal axes. The six possible spectra were simulated by using the shielding values in Table I for cyclopropane and the X-ray[7] bond length of 1.510 Å (D = 2200 Hz). The experimental spectrum obtained from a 1% mixture of 90% enriched cyclopropane-*1,2*-^{13}C in argon at 20 K corresponded with only one of the six possible ^{13}C shift tensor orientations. A slightly better agreement was obtained by using D = 2120 Hz or r = 1.53 Å, which still agrees with the X-ray result within the estimated error of $\pm$100 Hz for D. The apparently slightly longer bond length is probably due to the neglect of minor motional corrections.[3] The theoretical spectrum which agreed best is given in Figure 1 along with the experimental results. Of the remaining theoretical spectra corresponding to the five permutations of geometrical axes among the three experimental tensorial shift values, only one was at all similar to the experimental spectral pattern. This one also places σ_{33} along the same molecular axis but reverses the assignments of σ_{11} and σ_{22}. This alternative fit, however, was definitely inferior to that portrayed in Figure 1.

The proper orientation of the shift tensor places σ_{11} along the C_2 axis, σ_{22} perpendicular to the H–C–H moiety and σ_{33} perpendicular to the plane of the molecule. These results are especially interesting as the order and magnitude of σ_{11} and σ_{22} compare very well with the methylene values corresponding to similar geometrical orientations found in the single-crystal work on *n*-eiconsane.[8] On the other hand, the component perpendicular to the C–C–C plane in the previous work[8] is at lowest field but in cyclopropane it appears as σ_{33} at highest field. The reversal in order of this one unique component further dramatizes the unusual nature of these results. A shielding component along a given axis is basically determined by circulation of electrons in the plane perpendicular to the axis and containing the nucleus. Therefore, circulations of electrons in the cyclopropane molecular plane will give rise to the most unusual σ_{33} component. The σ_{22} shift is very similar to that in methane, as might be expected for a component perpendicular to the H–C–H plane (see also ref 8). The σ_{11} component along the C_2 axis samples electrons from both the C–C and C–H bonds in a sufficiently complex manner that no simple comparisons are made.

As the σ_{33} shifts are at extremely high fields for the methylenes in both of the three-membered rings reported here, the assignment of σ_{33} perpendicular to the plane of the molecules is probably correct also in cyclopropene. Molecular orbital calculations of the chemical shielding in these systems is currently under way in this laboratory, with the hope of providing a firmer theoretical understanding of these unique shifts.

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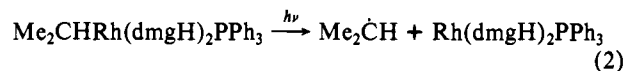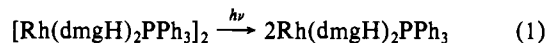(8) VanderHart, D. L. *J. Chem. Phys.* **1976**, *64*, 830.

Thermal and Photochemical Studies of a Monomeric Rhodium(II) Radical

Ursula Tinner and James H. Espenson*

Ames Laboratory and Department of Chemistry
Iowa State University
Ames, Iowa 50011

Rhodium(II) complexes, including those called rhodoximes,[1,2] do not normally occur as mononuclear species but rather in dinuclear forms containing a Rh–Rh single bond.[3] The particular complex of interest here is Rh(dmgH)$_2$PPh$_3$, a very reactive, 5-coordinate, 17-electron species. This previously unknown metal radical can be generated photochemically[4] from the stable dimeric rhodium(II) rhodoxime,[3] [Rh(dmgH)$_2$PPh$_3$]$_2$, and also from organorhodoximes such as *i*-C$_3$H$_7$Rh(dmgH)$_2$PPh$_3$. Irradiation into the visible absorption bands[5,6] of either compound causes homolytic dissociation of the Rh–Rh or Rh–C bond, respectively:

$$[\text{Rh(dmgH)}_2\text{PPh}_3]_2 \xrightarrow{h\nu} 2\text{Rh(dmgH)}_2\text{PPh}_3 \qquad (1)$$

$$\text{Me}_2\text{CHRh(dmgH)}_2\text{PPh}_3 \xrightarrow{h\nu} \text{Me}_2\dot{\text{C}}\text{H} + \text{Rh(dmgH)}_2\text{PPh}_3 \qquad (2)$$

Flash photolysis[4] of argon-blanketed solutions of either compound[7] in ethanol produced a chemical transient which is taken to be the same species, the mononuclear Rh(II) complex in both, on the basis of the following spectroscopic and kinetic evidence. When the Rh(II) dimer was used, its spectrum was recovered after decay of the transient in nearly quantitative yield. When the organorhodoxime was used, the dimer—a stable species under these conditions, easily recognized by its characteristic absorption spectrum—was produced both by flash and by continuous photolysis. The absorption spectrum of the transient itself could not be determined because it absorbs in the visible region much less than either of its precursors, and the degree of conversion is under 10%.

The transient decays by second-order kinetics according to the reverse of eq 1, with the same value of the rate constant from both. The observed second-order rate constant for dimerization (k_d) increases with the concentration of additional triphenylphosphine. The analysis of this dependence (Figure 1) suggests a mechanism in which four-coordinate and five-coordinate rhodium(II) species[8]

(1) Bis(dimethylglyoximato)rhodium complexes are referred to as "rhodoximes" by analogy to cobaloximes: Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97. dmgH$^-$ is the monoanion of 2,3-butanedione dioxime (or dimethylglyoxime).
(2) Schrauzer, G. N.; Weber, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 726.
(3) Caulton, K. G.; Cotton, F. A. *J. Am. Chem. Soc.* **1971**, *93*, 1914.
(4) The photolysis apparatus was based on the Model 710 system from the Xenon Corporation using FP-5-100c fast extinguishing flash tubes. In these studies a typical flash energy was 90 J, and the complexes were protected from UV irradiation by using Pyrex filters or jackets containing saturated aqueous sodium nitrite. Further information is given by: D. A. Ryan, Ph.D. Thesis, Iowa State University, 1981.
(5) The Rh(II) dimer has an intense absorption band centered at 452 nm, with $\epsilon \sim 5 \times 10^4$ M^{-1} cm^{-1}. The quantum yield is 0.015 $\pm$ 0.005 determined by using Cr(urea)$_6^{3+}$ actinometry [Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394] when solutions were filtered by using saturated sodium nitrite and Cu(NH$_3$)$_4^{2+}$ solutions. This system was chosen because its absorption spectrum matched that of the dimer in the region of light transmitted by the filters, with suitable adjustment of [Cr(urea)$_6^{3+}$] to give the same absorbance as the rhodium solution.
(6) Isopropyl(triphenylphosphino)rhodoxime has absorption maxima at 420 (sh), 333 (7.4 $\times$ 10^3), and 280 nm (1.3 $\times$ 10^4 M^{-1} cm^{-1}).
(7) 1-Octene was added to the solution of the isopropylrhodoxime to capture the 2-propyl radical preventing recombination by the reverse of reaction 2.
(8) Rhodium(II) species having coordination numbers of five and four have been recognized previously as reaction intermediates: (a) Lilie, J.; Trimme, M. G.; Endicott, J. F. *Inorg. Chem.* **1975**, *14*, 2129. (b) Miskowski, V. M.; Sigal, I. S.; Mann, K. R.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 4383. (c) Kelley, T. L.; Endicott, J. F. *Ibid.* **1972**, *94*, 1797.