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

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

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

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

where these parameters are given in Hz with $D$ and $J$ as the direct and indirect dipolar coupling constants, respectively. Both $\nu_1$ and $\nu_2$ 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 $\theta$ 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 ±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 $\sigma_{33}$ along the same molecular axis but reverses the assignments of $\sigma_{11}$ and $\sigma_{22}$. This alternative fit, however, was definitely inferior to that portrayed in Figure 1.

The proper orientation of the shift tensor places $\sigma_{11}$ along the $C_2$ axis, $\sigma_{22}$ perpendicular to the H–C–H moiety and $\sigma_{33}$ perpendicular to the plane of the molecule. These results are especially interesting as the order and magnitude of $\sigma_{11}$ and $\sigma_{22}$ compare very well with the methylene values corresponding to similar geometrical orientations found in the single-crystal work on *n*-eicosane.[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 $\sigma_{33}$ 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 $\sigma_{33}$ component. The $\sigma_{22}$ 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 $\sigma_{11}$ 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 $\sigma_{33}$ shifts are at extremely high fields for the methylenes in both of the three-membered rings reported here, the assignment of $\sigma_{33}$ 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.

**Acknowledgment.** Principal support was provided by the Chemistry Section of the National Science Foundation (Grants CHE-8000256 and CHE-7913781).

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

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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 $Rh(dmgH)_2PPh_3$, 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] $[Rh(dmgH)_2PPh_3]_2$, and also from organorhodoximes such as *i*-$C_3H_7Rh(dmgH)_2PPh_3$. Irradiation into the visible absorption bands[5,6] of either compound causes homolytic dissociation of the Rh–Rh or Rh–C bond, respectively:

$$[Rh(dmgH)_2PPh_3]_2 \xrightarrow{h\nu} 2Rh(dmgH)_2PPh_3 \qquad (1)$$

$$Me_2CHRh(dmgH)_2PPh_3 \xrightarrow{h\nu} Me_2\dot{C}H + Rh(dmgH)_2PPh_3 \qquad (2)$$

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]

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(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 ± 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 ($\epsilon$ 7.4 × $10^3$), and 280 nm (1.3 × $10^4$ $M^{-1}$ $cm^{-1}$).

(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.

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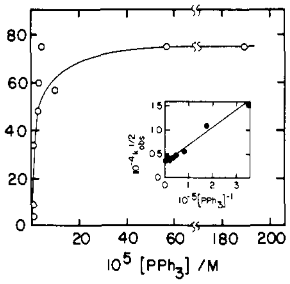

**Figure 1.** Illustrating the phosphine dependence of the observed pseudo-second-order rate constant for dimerization according to eq 5.

exist in equilibrium, but only the latter is reactive toward dimer formation:

$$Rh(dmgH)_2 + PPh_3 \overset{K_{45}}{\rightleftharpoons} Rh(dmgH)_2PPh_3 \qquad (3)$$

$$2Rh(dmgH)_2PPh_3 \xrightarrow{k_{55}} [Rh(dmgH)_2PPh_3]_2 \qquad (4)$$

$$-\frac{d[Rh(dmgH)_2PPh_3]}{2dt} = \frac{k_{55}}{(K_{45}^{-1}[PPh_3]^{-1} + 1)^2}[Rh(dmgH)_2PPh_3]^2 \qquad (5)$$

A least-squares analysis of the dependence of $k_d$ upon [$PPh_3$] according to eq 5 affords the values $2k_{55} = 7.5 \times 10^8$ $M^{-1}$ $s^{-1}$ and $K_{45} \sim 10^5$ $M^{-1}$. We conclude that the pathway shown by eq 4 predominates over those in which the reactants are two four-coordinate Rh(II) species or one of each (i.e., $k_{55} >> k_{44}, k_{45}$).

Further corroboration that the transient is indeed, the indicated monomeric rhodium(II) complex came from trapping experiments with such reagents as iron(III) chloride. These studies were necessarily limited to the use of the organorhodoxime as the starting material, since the rhodium(II) dimer reacts thermally as discussed below. Addition of iron(III) chloride prior to photolysis of isopropylrhodoxime results in total conversion of the transient to a rhodium(III) complex, chloro(triphenylphosphine)rhodoxime:

$$Rh(dmgH)_2PPh_3 + FeCl_3 \rightarrow ClRh(dmgH)_2PPh_3 + FeCl_2 \qquad (6)$$

A thermal reaction between the dimer and iron(III) chloride also occurs (eq 7). The reaction rate, easily determined by using

$$[Rh(dmgH)_2PPh_3]_2 + 2FeCl_3 = 2ClRh(dmgH)_2PPh_3 + 2FeCl_2 \qquad (7)$$

conventional techniques, is first order with respect to the concentration of the dimer but independent of [$Fe^{3+}$] ($9 \times 10^{-5} - 1.8 \times 10^{-3}$ M), [$H^+$], and [$Cl^-$]. The rate constant is $k_1 = 5.8 \times 10^{-2}$ $s^{-1}$ (ethanol, 25.0 °C) or $9.8 \times 10^{-2}$ $s^{-1}$ (THF, 25.0 °C). Determinations of the rate constant as a function of temperature (8-25 °C) in ethanol yield the activation parameters $\Delta H_1^* = 85.6 \pm 2.6$ kJ $mol^{-1}$ and $\Delta S_1^* = 19.2 \pm 7.7$ J $mol^{-1}$ $K^{-1}$. Use of $Fe(NO_3)_3$, $Fe(ClO_4)_3$, or $Fe(phen)_3Cl_3$ gave identical rate constants, although after consumption of the Rh(II) dimer was complete, further small absorbance changes were noted which could be attributed to substitution reactions of an axial ligand on the Rh(III) rhodoxime product. The kinetic data are explained by a mechanism consisting of the rate-limiting thermal dissociation of the dimer (eq 1) followed by its rapid oxidation (eq 6). On the basis of the value of $k_1$ and $k_{55}$ for eq 4, the equilibrium constant[9] between dimer and monomer in ethanol is $1.5 \times 10^{-10}$ M at 298 K, with $\Delta S° \sim 100$ J $mol^{-1}$ $K^{-1}$ and $\Delta H° \sim 86$ kJ $mol^{-1}$. The large positive value of $\Delta S°$ is consistent with the monomerization process.

If solvent effects are ignored, the estimate of $\Delta H°$ may be taken as an estimate of the metal-metal bond dissociation enthalpy in the dirhodium complex for which the Rh-Rh bond distance[3] is 2.97 Å. By way of comparison the bond energies and bond lengths of other Rh-Rh bonds are rhodium metal,[10] 93 (2.68); $Rh_4(CO)_{12}$, 91[11] and 114[10] (2.73); $Rh_6(CO)_{16}$, 89[11] and 114[11] kJ $mol^{-1}$ (2.78 Å). Comparisons with other dimeric $d^7$ complexes can also be made: the mass spectrometric value[12] for homolytic dissociation of $Tc_2(CO)_{10}$ is 177 kJ $mol^{-1}$, compared to $\Delta H^* = 160$ kJ $mol^{-1}$ from a kinetic study in decalin[13]. That the Tc-Tc bond is much stronger than the Rh-Rh bond is not unexpected in view of the much smaller degree of ligand-ligand repulsions in the former.[14]

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[9] The rate constants for the dimer (D) to monomer (M) interconversion are those defined by the rate law

$$-d[D]/dt = d[M]/2dt = k_1[D] - k_{55}[M]^2$$

The equilibrium constant for the reaction D ⇌ 2M is $K = k_1/k_{55}$.

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# Synthesis and Molecular Structure of the Dissymmetric Mo≡Mo Compound [($\eta^5$-$C_5H_5$)$_2$$Mo_2(CO)_3$($C_6H_5P(OCH_2CH_2)_2NH$)]: First Example of Direct CO Substitution in [($\eta^5$-$C_5H_5$)$Mo(CO)_2$]$_2$

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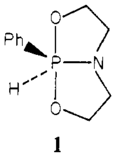
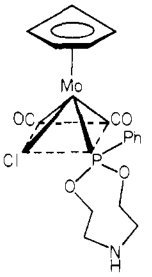
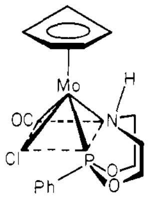
The bicyclophosphorane **1** (phoran) is the precursor of a multidonor site ligand, which, in its open tautomeric form, was found to coordinate transition metals[1] either via the triply coordinated phosphorus alone, as in **2**, or via both the triply coordinated phosphorus and nitrogen atoms as in 3. More recently, the



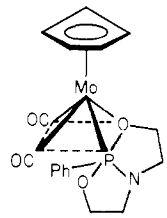
**1**



**2**



**3**



**4**

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