

Bond Character and Conformational Equilibration of Ethylene- and Tetrafluoroethylenerrhodium Complexes from Nuclear Magnetic Resonance Spectra¹

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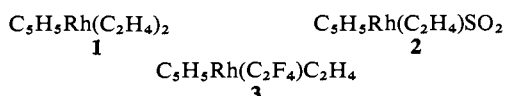
Abstract: The nuclear magnetic resonance spectra of π -cyclopentadienyldiethylenerrhodium (**1**), π -cyclopentadienylethylene(sulfur dioxide)rhodium (**2**), and π -cyclopentadienylethylenetetrafluoroethylenerrhodium (**3**) have been analyzed in terms of chemical shifts and coupling constants. There is relatively small difference between the proton-proton couplings, but a larger difference between fluorine-fluorine couplings of the coordinated and free alkenes, which suggests that coordination with rhodium produces a sizable change in hybridization of tetrafluoroethylene carbons. " π -Alkene complex" may be a misnomer for **3**. The barrier to rotation of the ethylenes in **1** about the carbon-rhodium bonds has been reinvestigated and found to have an activation energy of 15.0 ± 0.2 kcal/mol instead of about 6 kcal as previously reported. The E_a value for rotation of the ethylene in **2** is substantially less, 12.2 ± 0.8 kcal/mol, while that of **3** is somewhat more than for **2**, 13.6 ± 0.6 kcal/mol. Rotation of coordinated tetrafluoroethylene does not appear to be detectable up to 100° , the point where **3** begins to decompose.

The complexes of alkenes with transition metals are usually characterized as π complexes⁵ in which the $2p\pi$ orbitals of the alkene are taken to be involved in bond formation to the metal. Whether or not the hybridization of the carbons is changed sufficiently to warrant characterizing the bonds as being of the σ type is not yet clear and, of course, the situation may well be different for different complexes.

While a number of criteria of bond type might be used to characterize the carbon-metal bonds in alkene-metal complexes, we will be concerned here with the degree of similarity between the nmr coupling constants in free and bound alkenes in some alkene-rhodium complexes. The premise is that a large change in the internal couplings in the alkene on complex formation would indicate a substantial change in hybridization of the carbons attending carbon-metal bond formation. Along with the analyses of the nmr spectra we have investigated further the rates and activation energies for rotation of coordinated ethylene.^{6,7}

Analyses of Nmr Spectra of Alkene-Rhodium Complexes

π -Cyclopentadienyldiethylenerrhodium (**1**)^{6,8} shows



three principal proton nmr absorption peaks at room

temperature in methylene chloride solution: a sharp singlet at 5.5 ppm arising from the cyclopentadienyl hydrogens, and two broad, rather featureless peaks centered approximately on 1.23 and 3.12 ppm. The broad peaks arise from pairs of nonequivalent coordinated ethylene protons which are undergoing rotation at an intermediate rate on the nmr time scale.⁶ These peaks show substantial fine structure at -25° where rotation is slow (Figure 1). The spectrum is essentially of the AA'XX' type but doubled by coupling with ^{103}Rh (spin $1/2$). There is a slight deviation from symmetry of the two halves because the rhodium-proton splittings are slightly greater (2.4 Hz vs. 1.8 Hz) for one group of protons than for the other. Analysis of the spectrum by the method of Swalen and Reilly⁹ gave a set of chemical shift and coupling parameters (Table I) which reproduced all the observed spectral line positions to ± 0.06 Hz. The theoretical spectrum corresponding to these parameters is shown for comparison in Figure 1, and the intensities are also seen to fit well. A similar analysis of the resonances of coordinated ethylene in π -cyclopentadienylethylene(sulfur dioxide)rhodium (**2**)⁷ gave spectral parameters (Table I), which except for the chemical shifts, are very similar to those for **1** and gave a comparably good fit between line positions and intensities (Figure 2).

The changes in the internal coupling constants of ethylene which occur on coordination with rhodium are not especially large. It is interesting that the changes in the geminal couplings (J_{14}) are about 20% in the right direction toward what is commonly found for a saturated geminal methylene. The general correlation of the couplings in the complex with those of free ethylene is in keeping with the "inner and outer" chemical shift assignments made for **1**.⁶ Thus, if the pairs of equivalent hydrogens are the α,α and β,β pairs of ethylene, rather than α,β (*cis*) and α',β' (*cis*), a very large

(1) The part of this research carried on at the California Institute of Technology was supported by the National Science Foundation.

(2) Central Research Department of Du Pont.

(3) California Institute of Technology.

(4) Participant in the Undergraduate Research Program of the National Science Foundation.

(5) M. J. S. Dewar, *Bull. Soc. Chim. France*, **18**, C79 (1951); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(6) R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964).

(7) R. Cramer, *ibid.*, **89**, 5377 (1967).

(8) R. B. King, *Inorg. Chem.*, **2**, 528 (1963).

(9) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

Table I. Chemical Shift and Coupling Parameters for Coordinated Ethylenes in Ethylene-Rhodium Complexes
$$\begin{matrix} (1)X \\ (4)X' \end{matrix} > C=C < \begin{matrix} X(2) \\ X'(3) \end{matrix}$$

Compound	Chemical shifts, Hz		J_{12} , Hz	J_{34} , Hz	J_{13} , Hz	J_{14} , Hz	J_{15} , ^a Hz	J_{35} , ^a Hz
	1,2 ^b	3,4 ^b						
$C_5H_5Rh(C_2H_4)_2$	-72.4 ^c	-185.1 ^c	8.8	8.8	12.2	-0.06	1.8	2.5
$C_5H_5Rh(C_2H_4)SO_2$	-160.9	-232.0	8.8	8.8	14.4	-0.07	1.8	2.4
$C_5H_5Rh(C_2H_4)C_2F_4$	2160.0 ^d	3000.0 ^d	∓ 2.1	± 1.8	-48.6	128.7	4.9	8.3
Ethylene ^e	-152.4 ^e	-225.6 ^e	~ 8	~ 8	~ 13	~ 13	~ 13	~ 13
Tetrafluoroethylene			11.7		19.7	2.4	267	35.5
			74.3 ^h		-111.7 ^h	123.8 ^h	267.0 ^{h,j}	35.5 ^{h,k}
			75.3 ⁱ		-112.4 ⁱ	129.0 ⁱ	268.8 ^{h,j}	56.8 ^{h,k}

^a Rhodium-hydrogen coupling. ^b 1,2 = X(1),X(2) and 3,4 = X(3),X(4). ^c Relative to tetramethylsilane. ^d ¹⁹F in benzene relative to 1,2-difluoro-1,1,2,2-tetrachloroethane. ^e Ethylene protons relative to tetramethylsilane. ^f The spectrum was not well enough resolved to determine this coupling. ^g Values from N. Sheppard and R. M. Lynden-Bell, *Proc. Roy. Soc. (London)*, **A269**, 385 (1962). ^h Value based on iterative solution with coincidences at ± 155 Hz. ⁱ Value based on iterative solution with coincidences at ± 165 Hz. ^j J_{13CF} . ^k J_{13CCF} .

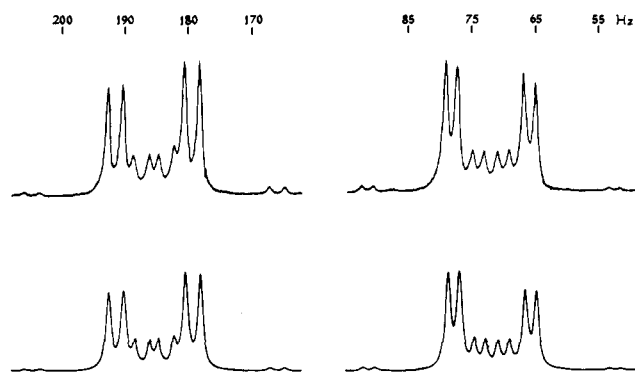


Figure 1. Proton nmr spectrum at 60 MHz of coordinated ethylene in $C_5H_5Rh(C_2H_4)_2$ at -25° in methylene chloride relative to tetramethylsilane as internal standard. Upper curves are the experimental spectrum while the lower curves were calculated using the parameters shown in Table I.

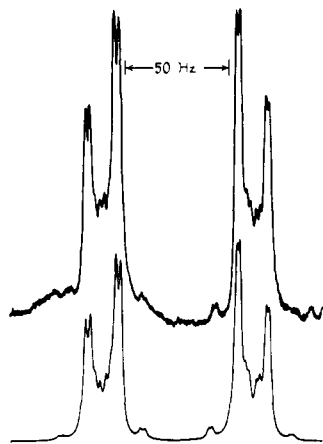


Figure 2. Experimental (upper) and calculated (lower) proton spectra at 60 MHz for $C_5H_5Rh(C_2H_4)SO_2$ at -50° in liquid sulfur dioxide; the band center is 196 Hz downfield from internal tetramethylsilane. The parameters for the calculated spectrum are given in Table I.

change in hybridization would have to occur, and if this were in the direction of making the carbons more sp^3 -like, the normal expectation would be to have J_{12} and J_{13} with opposite signs, a situation which would not give the proper nmr resonance intensities.

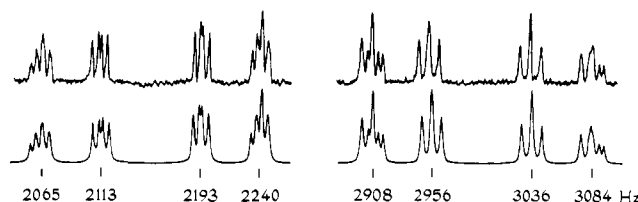
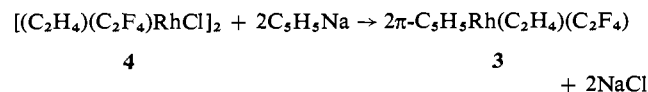


Figure 3. Experimental and calculated ¹⁹F spectrum at 56.4 MHz of π -cyclopentadienyltetrafluoroethylenerrhodium in benzene. Line positions are relative to 1,2-difluoro-1,1,2,2-tetrachloroethane.

Special interest attaches to the properties of ethylenes carrying electronegative substituents in their rhodium(I) complexes. These compounds tend to be more stable than complexes of comparable unsubstituted alkenes,¹⁰ and this enhanced stability was explained in terms of a modified π bond. It is, however, a currently unsettled question whether this formulation is the most satisfactory one for complexes of alkenes with extreme electronegative substitution. Among such alkenes tetrafluoroethylene is a prime example and, like ethylene, is amenable to nmr analysis. Although tetrafluoroethylene complexes may be obtained by displacement of coordinated ethylene from some rhodium(I) compounds,¹¹ this is not possible with **1**, which is inert to nucleophilic reagents.⁶ Accordingly, **3** was prepared by the following reaction, the starting material for which, **4**, has been previously described.¹¹



The ¹⁹F resonance spectrum of **3** is quite complex (Figure 3) and could only be fitted by taking account of the signs of all the couplings except those to rhodium (see Table I).

A problem arises here with respect to whether or not to take the largest FF coupling to correspond to a *gem* coupling or a *trans*-alkenic coupling. The first choice corresponds to the numbering scheme of **4** and the second

(10) R. Cramer, *J. Am. Chem. Soc.*, **89**, 4621 (1967).

(11) R. Cramer and G. W. Parshall, *ibid.*, **87**, 1392 (1965).

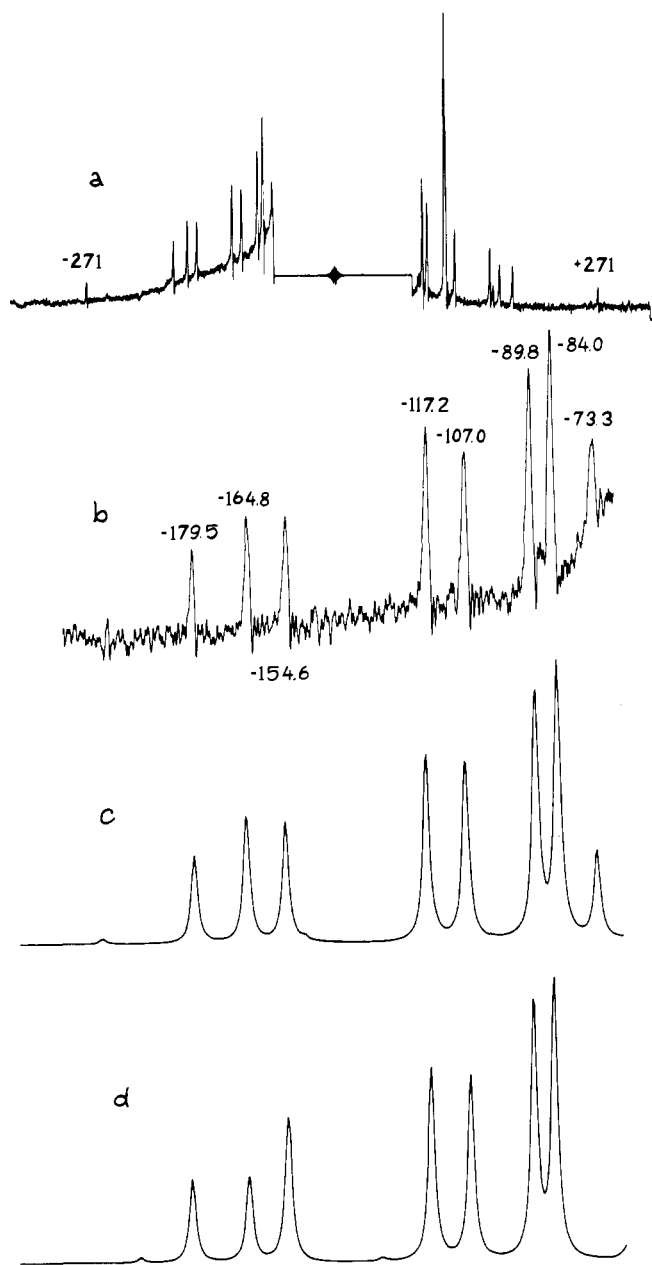
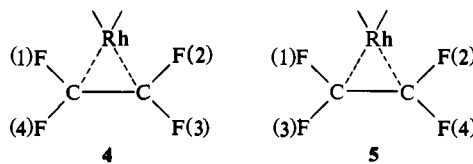


Figure 4. ^{13}C satellite spectra at 94.1. MHz of neat tetrafluoroethylene at -70° . The spectrometer was locked on the center-band fluorine resonances. (a) Full spectrum showing some impurity lines and lines at ± 271 Hz which were assigned to anti-symmetric transitions (see text). (b) Part of downfield half of spectrum on a narrower sweep; the peak at -73.3 Hz is not surely a ^{13}C satellite peak. (c) Partial calculated spectrum assuming coincidences at ± 165 Hz. (d) Partial calculated spectrum assuming coincidences at ± 155 Hz. The parameters which give spectra c and d give antisymmetric transitions at ± 271 Hz of the proper intensities.

to **5** as regards the data in Table I. We feel **4** to be more reasonable because, as will be shown later, the couplings in the coordinated tetrafluoroethylene differ substantially from those of tetrafluoroethylene. If the orientation with respect to the cyclopentadienyl group of coordinated tetrafluoroethylene corresponds to that of ethylene, fluorines 1 and 2 are equivalent and 3 and 4 are equivalent. But the J_{12} and J_{34} couplings are small, reminiscent of vicinal saturated couplings, and to



the general degree which these couplings become smaller, we expect the *gem* couplings (J_{14} , J_{23}) to become larger, as in saturated CF_2 compounds. Typical values are 157 (1-methyl-2,2-difluorocyclopropane),¹² 260 (1-phenyl-2,2,3,3-tetrafluorocyclobutane), and 240 Hz (1,1-difluorocyclohexane).¹³

In accord with studies of fluorinated compounds¹⁴ and assignment **4**, the J_{13} coupling was taken to be negative. The differences in sign between J_{13} and J_{14} and between J_{12} and J_{34} are both required for a satisfactory fit.

For comparison with the FF couplings in **3**, the internal FF couplings in tetrafluoroethylene were desired, and about the only satisfactory way to obtain these is either from the ^{13}C satellites on the ^{19}F spectrum of tetrafluoroethylene or from the ^{13}C spectrum itself. Observation of the ^{13}C spectrum with natural-abundance ^{13}C was not possible because of the difficulty in obtaining high enough tetrafluoroethylene concentrations at room temperature. On the other hand, analysis of the ^{13}C satellites on the ^{19}F spectrum, which could be obtained with a reasonable signal-to-noise ratio at -70° , is complicated by the large FF couplings which are comparable to the ^{13}CF couplings. The result is that some of the stronger satellite lines fall too close to the center peak for observation. Nonetheless, a reasonably good analysis of the satellite spectrum was achieved which, because the procedure had some not-straightforward elements, will be described in detail.

The principal features of the ^{13}C satellites on the ^{19}F spectrum of tetrafluoroethylene are shown in Figure 4. Part of the problem was to identify the peaks which belonged to the satellite spectrum and which were due to impurities, spinning side bands, or other artifacts. The best criterion seemed to be symmetry of location, which, fortunately, was not with respect to the center of the $^{12}\text{CF}_2=^{12}\text{CF}_2$ resonance but a point 9 Hz (0.1 ppm) upfield from it because of a ^{13}C isotope effect on the ^{19}F chemical shift. All peaks were disregarded which did not have a counterpart on each side of the ^{13}C satellite spectrum.

A preliminary trial of FF and ^{13}CF coupling constants for reasonably analogous compounds such as $\text{F}_2\text{C}=\text{CFCl}$ gleaned from the literature¹⁴ using the first stage of the LAOCOON II program¹⁵ reproduced the general features of the spectrum, although showing rather more medium-intensity lines than were actually observed. In assigning the observed transitions to changes between specific energy levels of the $\text{AA}'\text{BB}'\text{X}$ system,¹⁶ the one almost

(12) W. D. Phillips, *J. Chem. Phys.*, **25**, 949 (1956).

(13) S. L. Spassov, D. L. Griffith, E. S. Glazer, K. Nagarajan, and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 88 (1967).

(14) See, for examples, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, pp 875-889, 906-916.

(15) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

(16) Some notation such as this with $\text{AA}'\text{BB}'$ as fluorines and X as ^{13}C is required because even though the only chemical shift difference between A and B is the result of the 9-Hz isotope effect, $J_{\text{AX}} \neq J_{\text{BX}}$.

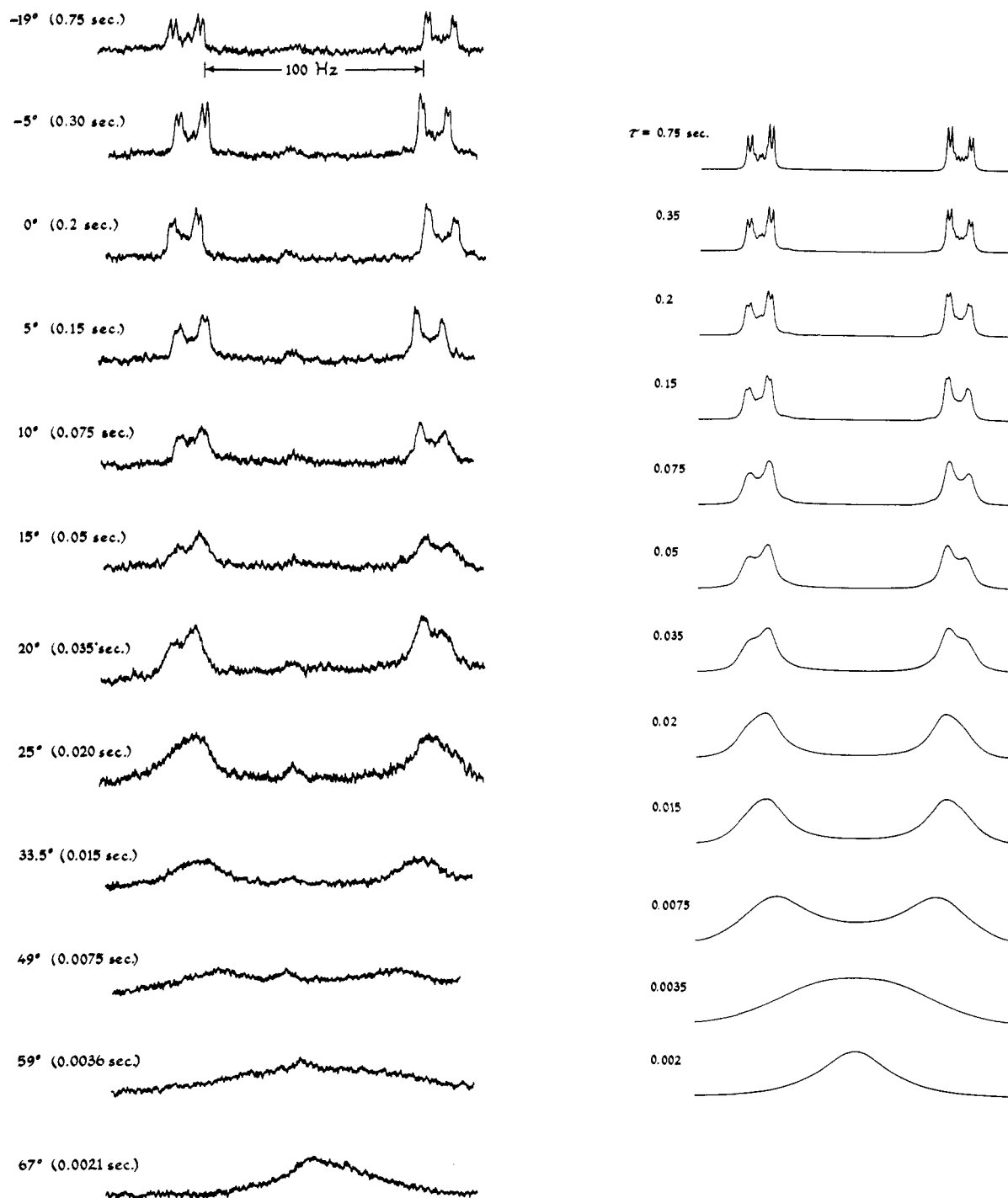


Figure 5. Left side, variation of the 60-MHz proton spectrum of π -cyclopentadienyldiethylenrhodium in deuterioacetone with temperature. Right side, theoretical spectra calculated as a function of τ by the procedure described in the text. The calculated spectra do not exactly match the experimental spectra because they have been normalized to a constant maximum signal strength.

unambiguous assignment was of the rather sharp resonances at ± 271 Hz to the antisymmetric transitions which correspond to $2a'_0 \rightarrow 2a'_1$ and $2a'_{-1} \rightarrow 1a'_0$ A-type transitions in the AA'BB' case where $M = 0$.¹⁷ Various assignments of the inner transitions $1a'_0 \rightarrow 2a'_1$ and

$2a'_{-1} \rightarrow 2a'_0$ were tested, and the best fit was obtained with ± 89 Hz. This requires that $J_{FF}(cis)$ be about 75 Hz, $J_{FF}(trans)$ be about -112 Hz, and J_{13CF} be about 267 Hz. These values are comparable to $J_{FF}(cis) = 58$ Hz and $J_{FF}(trans) = 115$ Hz for trifluorochloroethylene^{14,18} and $J_{13CF} = 299.3$ and 289.6 Hz for *cis*- and

(17) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 138-151.

(18) H. M. McConnell, C. A. Reilly, and A. D. McLean, *J. Chem. Phys.*, **24**, 479 (1956).

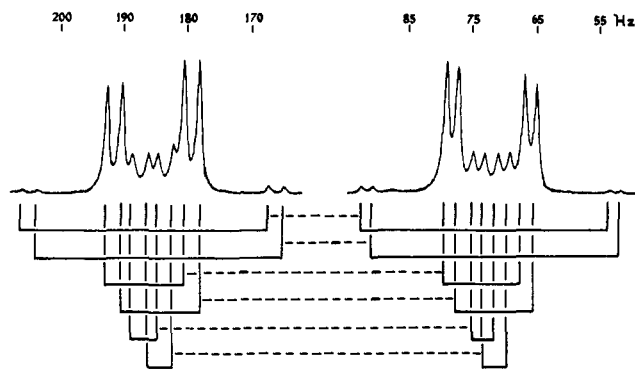


Figure 6. Diagram showing pairs of resonance lines considered as AB exchanging systems in approximate treatment of ethylene rotation in π -cyclopentadienyldiethylenorhodium (1).

trans-1,2-difluoro-1,2-dichloroethylenes, respectively.^{14,19} In finding values for the other couplings, a difficulty was encountered because the best partial fit to the parameters led to the expectation that the equal transitions corresponding to $1a'_{-1} \rightarrow 2a'_0$ and $1a'_0 \rightarrow 2a'_1$ should be clearly visible at about ± 159 Hz, and no small peak appears in this region. It was concluded that these transitions must be included in one or the other of the pairs of peaks at ± 155 or ± 165 Hz. Iterations based on these possibilities were carried out and gave comparably good fits, the root mean square error being 0.6 Hz for coincidence at ± 155 Hz and 0.4 Hz for coincidence at ± 165 Hz. Calculated curves for both sets of parameters are seen to compare well with the downfield half of the experimental spectrum in Figure 4. Because there is no clear way to decide between these sets of parameters, except by the general pattern of the intensities which favors assigning the coincidences at ± 165 Hz and uncertain close-in transitions, both are listed in Table I. Relative to trifluorochloroethylene, the couplings seem normal, except that $J_{FF(gem)}$ is quite large, 124–130 Hz compared to 78 Hz.

As noted earlier, and irrespective of whether assignment 4 or 5 is accepted, the changes in couplings attending the coordination of tetrafluoroethylene to rhodium are large, especially the *cis* vicinal couplings. This strongly suggests substantial differences in bond type, and if assignment 4 is correct, the changes are very much in the direction of what would be expected for a σ complex, a conclusion which is in accord with the reluctance of the C_2F_4 group to rotate in the same way as the ethylene group. The present evidence suggests that the designation π complex may well be a misnomer for the coordinated tetrafluoroethylene in 3.²⁰

Rates of Ethylene Rotation in Ethylene–Rhodium Complexes

The nmr spectrum of the protons of the ethylene coordinated to rhodium in 1 at ambient temperatures is

(19) G. V. D. Tiers and P. C. Lauterbur, *J. Chem. Phys.*, **36**, 1110 (1962).

(20) A similar conclusion has been reached for coordinated hexafluoropropene in bis(triphenylphosphine)hexafluoropropeneplatinum by M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *Chem. Commun.*, 502 (1966); see also B. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.*, **A**, 167 (1968).

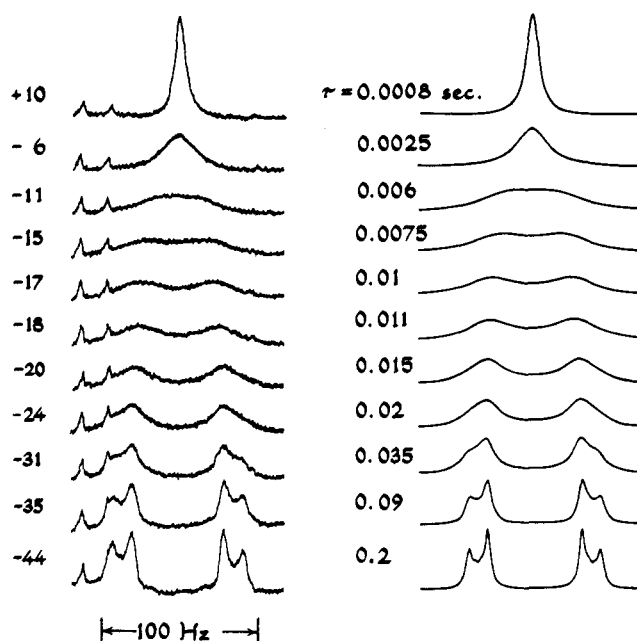


Figure 7. Left side, proton nmr spectrum of π -cyclopentadienyldiethylenetetrafluoroethylenorhodium (3) as a function of temperature in deuteriochloroform at 60 MHz. Right side, theoretical spectra calculated as a function of τ by the procedure described in the text.

relatively broad and featureless, but becomes a sharp AA'BB'X spectrum at low temperatures and a simple doublet with a 2.1-Hz spacing at 125° (the average of proton–rhodium couplings J_{15} and J_{35} in Table I).²¹ The changes which occur in the spectrum of 1 in deuterioacetone with temperature are shown in Figure 5. Previously,⁶ the changes in line positions as a function of temperature were used to calculate rates for rotation of the coordinated ethylenes. The activation energy so obtained (5.7 kcal/mol) is quite small for a process associated with a coalescence temperature of about 55° which, for a chemical shift difference of 110 Hz, corresponds to a mean lifetime before exchange of 0.002 sec. The reason for the small value is largely a decrease in $\delta\nu_\infty$ with temperature,²² the result being to make it appear that the rate is changing over a much longer range than in fact can be accurately measured by changes in line separations and hence make E_a appear to be too small.

The problem of developing theoretical line shapes as a function of τ is not a trivial one for an AA'BB'X system changing over, as the result of exchange, to an A_4X system. The approach taken here was an approximate one for which no theoretical justification can be supplied but which gives line shapes corresponding very closely to experiment. The procedure involved setting

(21) Observation of the average J_{15} and J_{35} coupling as 2.1 Hz strongly supports other evidence⁶ that intermolecular exchange of the ethylenes is not responsible for the rate effects on the spectra and furthermore shows that J_{15} and J_{35} have the same sign.

(22) Cf. J. D. Roberts, *Chem. Brit.*, 529 (1967). A clear tipoff that simple line-position measurements are unreliable for determining the rate of exchange with 1, because of a temperature-dependent $\delta\nu_\infty$, comes from the fact that the lines begin to move together *before* the peaks broaden enough to overlap. Theoretical line-shape analysis indicates that the true coalescence behavior should not be apparent until this degree of broadening has occurred.

up the AA'BB' system as a composite of six separate exchanging AB systems with different chemical shifts and couplings but with common τ values. The pairs of lines chosen for the individual exchanging AB pairs are shown in Figure 6. The line shapes were calculated for each AB system as described earlier,²³ then weighted and summed to obtain the composite spectrum. The weightings were adjusted to accord with the observed spectral intensities in the low-temperature extreme. Theoretical spectra calculated as a function of τ to match the experimental spectra are shown in Figure 5.

The general correspondence between calculated and experimental spectra is very good, especially in the region where exchange is slow ($\tau > 0.020$ sec). This is the critical region because, when τ is less than 0.020 sec, the subsequent changes in the spectrum almost to the high-temperature extreme are found to be well approximated by a single exchanging AB system with $\delta\nu_\infty = 113$ Hz and $J_{AB} = 12.2$ Hz. The approximate treatment permits matching of spectra over more than an order of magnitude larger variation in rate than would be otherwise possible. Unfortunately, the degree of temperature control and accuracy for the experimental curves shown in Figure 5 was not precise enough for satisfactory calculation of E_a for the rotation of ethylene. Another set of 18 curves obtained with the temperature calibrated by the procedure of Duerst and Merbach²⁴ and covering a rate range of a factor of 200 gave $E_a = 14.95 \pm 0.18$ kcal/mol and $\log A = 12.52$. The solvent for these spectra was methylene chloride.

Available variable-temperature spectra for cyclopentadienylethylene(sulfur dioxide)rhodium (**2**) were not of as good quality as those for **1**, but nine points covering a rate range of a factor of 12 gave $E_a = 12.2 \pm 0.8$ kcal and $\log A = 12.26$. The coalescence point for **2** is about -5° , which is some 50° less than that for **1** and

(23) S. Alexander, *J. Chem. Phys.*, **37**, 967, 974 (1962); **38**, 1787 (1963); **40**, 2741 (1964); J. L. Beauchamp, B.S. Thesis, California Institute of Technology, 1964. We are much indebted to Dr. J. T. Gerig for his assistance with the computer program used in this work.

(24) R. Duerst and A. Merbach, *Rev. Sci. Instr.*, **36**, 1896 (1965).

about 10° of which is due to the smaller chemical shift difference between the protons in the nonrotating coordinated ethylene.

More and better data were available for rotation in the ethylene coordinated in the ethylenetetrafluoroethylene complex **3**. The calculated and experimental curves for this compound are compared in Figure 7, and from eleven points, covering a range of rates over a factor of 250, $E_a = 13.6 \pm 0.6$ kcal and $\log A = 13.6$ were obtained. The coalescence point for **3** (about -10°) is somewhat lower than that for **2** but E_a seems to be a little larger than for **2**.

Formulation of the ethylene-rhodium bond in **2** and **3** as a π bond is consistent with the lower rotation barrier in these compounds. Electronegative ligands are expected to reduce the electron density of rhodium and thus weaken the back bond.

No change in the fluorine spectrum of **3** occurred up to 100° where decomposition began. Clearly the barrier to rotation of tetrafluoroethylene is much greater than of ethylene in **3**.

Experimental Section

π -Cyclopentadienylethylenetetrafluoroethylenrhodium (**3**). Crude μ -dichloro-diethyleneditetrafluoroethylenedirrhodium (**4**)¹⁰ from 4.0 g (10 mmol) of μ -dichloro-tetraethylenedirrhodium²⁵ was dissolved in tetrahydrofuran and a solution of 25 mmol of sodium cyclopentadienide in 25 ml of tetrahydrofuran was added under nitrogen in five portions over 30 min at 25° . Additional tetrahydrofuran (20 ml) was run in and the mixture stirred 1 hr longer at 25° . The solvent was removed under reduced pressure at 0° and the residue sublimed at $60-70^\circ$ (0.2 mm). The yield of sublimate was 1.7 g (28%).

The product could be crystallized from 30 ml of pentane at -80° , giving yellow needles which changed to cubes at 25° and melted at $76.5-77^\circ$.

Anal. Calcd for $C_9H_9F_4Rh$: C, 36.51; H, 3.06; F, 25.67. Found: C, 36.78; H, 3.14; F, 25.43.

The infrared spectrum (KBr wafer) had peaks at 3130 (w), 1950 (w), 1850 (w), 1645 (w), 1450 (s), 1409 (w), 1355 (w), 1227 (s), 1118 (s), 1054 (m), 1037 (s), 990 (w), 970 (m), 873 (w), 833 (w), 811 (s), and 785 (br, s) cm^{-1} .

(25) R. Cramer, *Inorg. Chem.*, **1**, 722 (1962).