

significance in many processes that are metal ion dependent.

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[CONTRIBUTION NO. 866, CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

Olefin Coordination Compounds of Rhodium: The Barrier to Rotation of Coordinated Ethylene and the Mechanism of Olefin Exchange

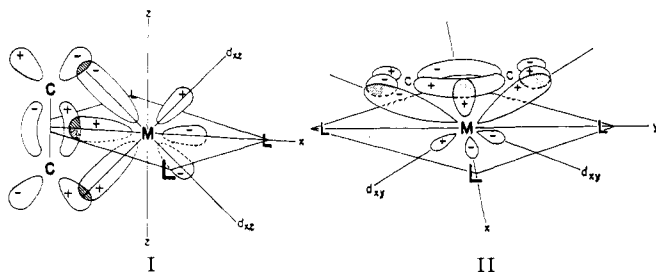
BY RICHARD CRAMER

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Coordinated olefins have generally been depicted as rigidly attached to metal ions with the olefin bond perpendicular to the coordination plane in 4-coordinate planar complexes. Nuclear magnetic resonance evidence is presented to show that ethylene coordinated to rhodium(I) in the compound $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ may rotate with the coordination bond as axis. The energy barrier to rotation is 6 kcal. Ethylene exchange with $(\text{CH}_3\text{COCHCOCH}_3)\text{Rh}(\text{C}_2\text{H}_4)_2$ is a bimolecular reaction. The difference in ability of $(\text{CH}_3\text{COCHCOCH}_3)\text{Rh}(\text{C}_2\text{H}_4)_2$ and $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ to undergo ethylene exchange is discussed in terms of the effective atomic number of rhodium in these compounds.

Introduction

Following Dewar¹ it has been customary² to describe the bond by which olefins are coordinated to transition metals as consisting of two parts (I): (a) a σ -bond, corresponding to the classical coordination bond, formed by overlap of the filled π -orbital of the olefin with a vacant metal orbital; and (b) a π -bond obtained through overlap of the vacant antibonding orbital of the olefin with a filled d -orbital of the metal.



X-Ray studies show that in crystalline $[(\text{C}_2\text{H}_4)\text{PdCl}_2]_2$,^{3a} $[(\text{C}_2\text{H}_4)\text{Pt}(\text{HN}(\text{CH}_3)_2)\text{Cl}_2]$,^{3b} $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]\cdot\text{H}_2\text{O}$,^{3c} and other platinum complexes,^{3d} the olefin double bond is perpendicular to the coordination plane as shown in I with the d_{xz} metal orbital involved in the π -bond. This geometry has been adopted generally for planar complexes containing olefins. However, it is also conceivable that the d_{xy} metal orbital could participate in a similar bond (II). It will be shown that the n.m.r. spectrum of $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ indicates that in this compound coordinated ethylene molecules rotate with the coordination bond as axis. The low energy barrier to rotation (6 kcal.) suggests that a structure such as II is involved.

Mechanism for the Equilibration of Ethylene Protons in Bis-(ethylene)- π -cyclopentadienylrhodium(I).—At 25° the proton n.m.r. spectrum of $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ ⁴ dissolved in chloroform has three maxima (see Fig. 1), a sharp peak at -5.15 p.p.m. (relative to tetramethylsilane), attributed to cyclopentadienyl protons, and broad absorptions centered at -2.77 and -1.12

p.p.m. due to protons of coordinated ethylene. Integration of the absorption signal shows that the ratio of the three kinds of protons is 5:4:4. The peak at -5.15 p.p.m. is split into a doublet (separation 0.8 c.p.s.) by rhodium. When the solution of the complex is chilled to -20° , the absorptions at -2.77 and -1.12 p.p.m. are each split into two pairs of doublets. If the solution is heated to 57° , the ethylene proton absorption bands converge into a single absorption at -1.93 p.p.m., corresponding to rapid proton equilibration at that temperature. Since it is highly probable that the coordinated ethylene molecules of $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ are equivalent, it appears that each ethylene ligand carries two protons of each type.

Several mechanisms may be considered for the equilibration of olefin protons in $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$: (1) Individual protons may exchange without disturbing the rhodium-ethylene coordination bond. (2) Protons may exchange by a nonclassical tunneling mechanism. (3) Ethylene molecules may exchange by a mechanism involving dissociation. (4) Coordinated ethylene molecules may exchange in a bimolecular reaction of $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ without dissociation of ethylene. (5) Depending upon the reason for nonequivalence of ethylene protons, rapid rotation of coordinated ethylene with either the olefin bond or the coordination bond as axis might lead to a single proton absorption.

These possible mechanisms have been assessed experimentally and the first four are excluded. It appears that rapid rotation with the coordination bond as axis is responsible for proton isomerization.

The first mechanism, exchange of olefin protons, was tested by heating solutions of $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ in CH_3OD and it was found that no H-D exchange occurred under conditions of rapid ethylenic proton equilibration. This result was confirmed by the discovery that olefin protons of an analogous compound $\text{C}_5\text{H}_5\text{Rh}(\text{CH}_2=\text{CHCH}_2-\text{CH}=\text{CH}_2)$ do not equilibrate at 100° . It is expected that the chelated structure of this complex could interfere with proton equilibration by rotation or olefin dissociation mechanisms but not by a hydrogen exchange mechanism.

The possibility of a tunneling mechanism was excluded when deuterium n.m.r. studies showed that deuterium equilibration in $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{D}_4)_2$ was substantially as fast as proton equilibration in $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$.

In examining the possibility of ethylene exchange by a dissociation mechanism, it was found that no exchange of coordinated C_2H_4 and free C_2D_4 occurred in 5 hr. at 100° , conditions far more rigorous than those required for hydrogen equilibration of complexed ethyl-

(1) M. J. S. Dewar, *Bull. soc. chim. France*, **18**, C79 (1951).

(2) (a) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 351; (b) G. E. Coates, "Organo-Metallic Compounds," 2d Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 343; (c) L. E. Orgel, "An Introduction to Transition-Metal Chemistry, Ligand Field Theory," John Wiley and Sons, Inc., New York, N. Y., 1960, p. 153.

(3) (a) J. N. Dempsey and N. C. Baenziger, *J. Am. Chem. Soc.*, **77**, 4984 (1955); (b) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *Acta Cryst.*, **13**, 149 (1960); (c) J. A. Wunderlich and D. P. Mellor, *ibid.*, **7**, 130 (1954); **8**, 57 (1955); (d) G. B. Bokii and G. A. Kukina, *Akad. Nauk S.S.S.R. Kryst.*, **2**, 400 (1957).

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

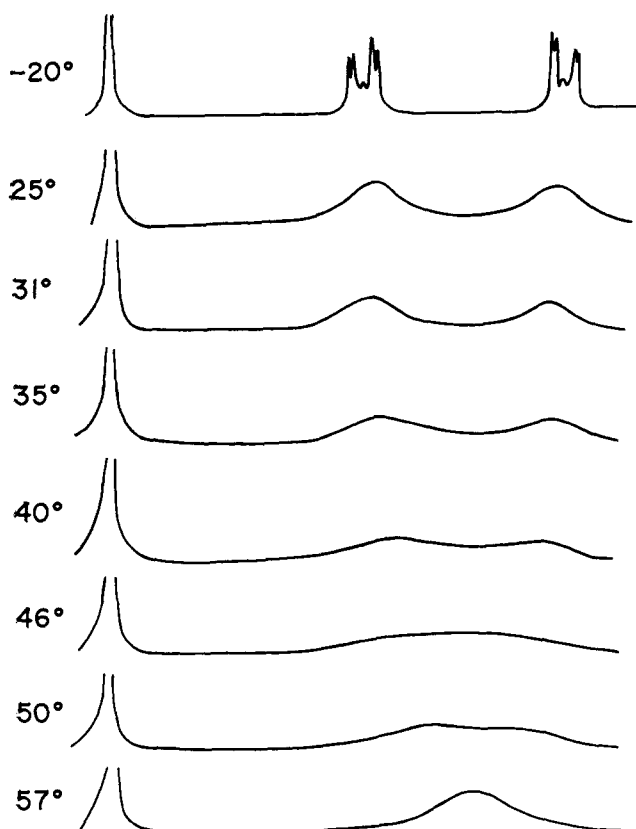


Fig. 1.—Temperature dependence of n.m.r. spectrum of $C_5H_5Rh(C_2H_4)_2$ in chloroform.

ene. It appears that a nondissociative ethylene exchange is also excluded, because the rate of proton equilibration does not increase with complex concentration as would be expected for a bimolecular reaction.

By elimination of other possibilities we are left with a rotation mechanism for proton isomerization. A comparison of the rotation mechanisms will be deferred until the evaluation of the rotation barrier has been discussed.

Ethylene Rotation Barrier in Bis-(ethylene)- π -cyclopentadienylrhodium(I).—If ethylene rotation is responsible for proton equilibration in $C_5H_5Rh(C_2H_4)_2$, the reorientation process would be expected to be first order, and the argument developed by Gutowsky and Holm⁵ for the quantitative study of hindered internal rotation by nuclear resonance is applicable.⁶ As the temperature of a solution of $C_5H_5Rh(C_2H_4)_2$ is raised, the apparent difference in the chemical shift values for the two kinds of ethylene protons decreases and, according to these authors, if the absorption line width is small compared to $\delta\omega$, the relationship between the chemical shift difference (at a temperature where exchange is appreciable) and the average lifetime of protons at each site at that temperature is given by the expression

$$\delta\omega_e = (1 - 2/\tau^2\delta\omega^2)^{1/2}\delta\omega \quad (1)$$

where $\delta\omega$ = chemical shift difference of protons at the two sites when exchange is negligible and there is no absorption overlap. $\delta\omega_e$ = chemical shift difference at temperature, t , at which exchange is appreciable. $\tau = \tau_A\tau_B/(\tau_A + \tau_B)$, where τ_A and τ_B are the average lifetimes of protons at sites A and B at temperature, t .

(5) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(6) The fact that the absorptions of the two kinds of ethylene protons are split may be considered to impair this treatment (see J. Kaplan, *J. Chem. Phys.*, **28**, 278 (1958), and S. Alexander, *ibid.*, **37**, 967 (1963)). However, the chemical shift difference (110 c.p.s.) is so much larger than the maximum splitting (12 c.p.s.) that we believe the calculations are valid.

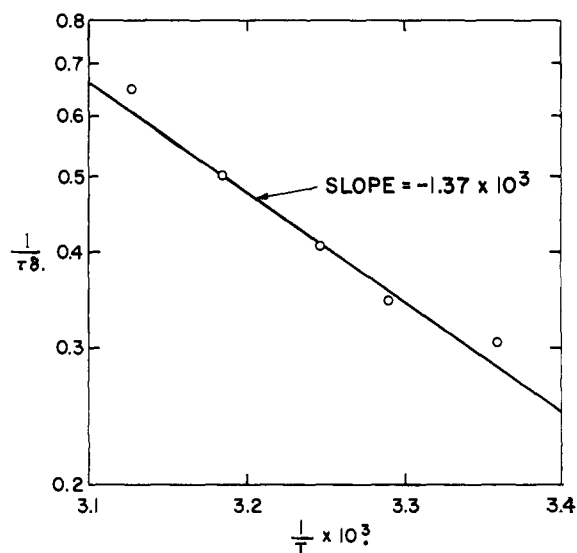


Fig. 2.—Effect of temperature on the chemical shift difference of ethylene protons of $C_5H_5Rh(C_2H_4)_2$ in chloroform solution.

A plot of $\log(1/\tau\delta\omega)$ at various temperatures against the corresponding value for $1/T$ should yield, for a unimolecular reaction, a straight line with a slope of $E_a/2.3R$ and an intercept at $1/T = 0$ whose value is $\log(2\nu_0/\delta\omega)$, where E_a = activation energy for rotation and ν_0 = frequency factor in the rate expression, $k = \nu_0 \exp(-E_a/RT)$. The temperature dependence of the proton n.m.r. spectrum of a chloroform solution of $C_5H_5Rh(C_2H_4)_2$ is shown in Fig. 1. Corresponding numerical values are summarized in Table I and are plotted in Fig. 2.

TABLE I
CHEMICAL SHIFT DIFFERENCES FOR ETHYLENE PROTONS IN $C_5H_5Rh(C_2H_4)_2$ AT VARIOUS TEMPERATURES

Temp. °C.	$\delta\omega_e$, cycles sec. ⁻¹	$1/\tau\delta\omega^a$	$1/T \times 10^3$
-20	110 ^b		
+25	99	0.31	3.36
31	96	.35	3.29
35	90	.41	3.25
40	78	.50	3.19
46	ca. 44	ca. .65	3.13
57	0		

^a $1/\tau\delta\omega = [1/2(1 - \delta\omega_e^2/\delta\omega^2)]^{1/2}$. ^b This value taken as $\delta\omega$.

The rate expression for rotation of ethylene in $C_5H_5Rh(C_2H_4)_2$ estimated from the slope and intercept of Fig. 2 is

$$k = 6.6 \times 10^6 \exp -6200/RT$$

Experiments in other solvents (Table II) give approximately the same values for the activation energy and frequency factor. If rotation is responsible for proton equilibration, the rate of equilibration would be expected to be relatively independent of the solvent.

TABLE II
ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR ETHYLENE ROTATION IN $C_5H_5Rh(C_2H_4)_2$ IN VARIOUS SOLVENTS

Solvent	E_a , cal.	ν_0 , sec. ⁻¹ $\times 10^{-5}$
Chloroform	6200	6.6
<i>d</i> ₆ -Acetone	5700	2.0
Toluene	6600	8.7

If the olefin bond of ethylene is the rotational axis, rotation will rupture both the π - and σ -coordination bonds. This should lead to dissociation which is not observed. Furthermore, the energy requirement for such a rotation would be expected to be much higher

than 6 kcal. Thus, the bond energy of the silver-olefin coordination bond has been given⁷ as 20–30 kcal. and the rhodium(I)-olefin bond appears to be stronger than the silver-olefin bond.

It is concluded that rotation of ethylene about the coordination bond is responsible for the convergence of the two olefin proton n.m.r. absorption bands. This rotation does not require that the π -coordination bond be broken.⁸ As the ethylene molecule rotates from a position vertical to the rhodium coordination plane (I), where π -bonding involves the d_{xz} metal orbital, to a coplanar orientation (II), where the d_{xy} metal orbital is utilized in π -bonding, it will pass through a sector in which both d_{xz} and d_{xy} metal orbitals participate in the π -bond thus facilitating ethylene rotation and accounting for the low energy barrier to rotation.

If the difference in infrared absorption attributed to the C=C stretching vibration of free and coordinated olefin is taken as a criterion of the strength of the coordination bond,⁹ then olefins are relatively strongly coordinated to rhodium(I), because the frequency depression for 1,5-hexadiene coordinated to Rh(I) is 160 cm^{-1} compared with ~ 140 cm^{-1} for olefin-Pt(II) complexes and 60 to 70 cm^{-1} for argentous complexes.

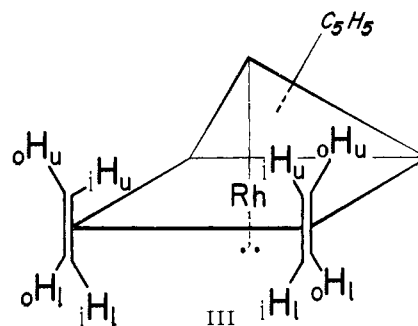
The rate of deuterium equilibration of $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{D}_4)_2$ dissolved in chloroform was estimated from the deuterium n.m.r. absorption pattern measured at 9.2 Mc. At 25° there was a single broad absorption (13.4 c.p.s. wide at half-height) located 20 c.p.s. upfield from D_2O (external). On cooling to about 0° this absorption was split into two peaks whose maxima were separated by 16 ± 1 c.p.s. Equipment was not available for accurately measuring and precisely controlling the temperature of the test solution. The rate of rotation of coordinated C_2D_4 in $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{D}_4)_2$ can be calculated, assuming it is the same as the rate of rotation of C_2H_4 in $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$, by the equation

$$k = 6.6 \times 10^5 \exp -6200/RT$$

The calculated half-life is 0.034 sec. at 25° (rotation rate 30 c.p.s.) and 0.089 sec. at 0° (rotation rate 11 c.p.s.).

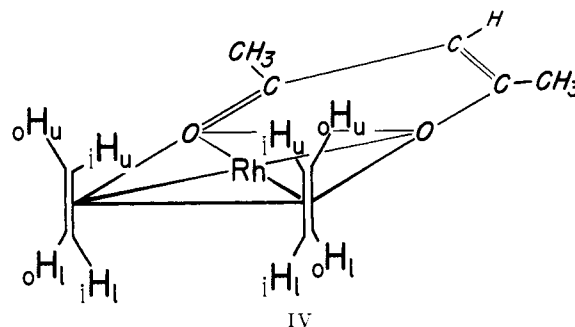
These calculations, assuming rotation of C_2D_4 as the cause of deuterium equilibration, conform with the found temperature dependence of the n.m.r. spectrum of $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_2\text{D}_4)_2$. If a tunneling effect were involved, equilibration of deuterium would have been substantially slower than equilibration of protons.

Identification of Protons in the N.m.r. Spectra of Olefin-Rhodium Coordination Compounds.—The n.m.r. spectrum of $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ shows that it contains two kinds of ethylene protons but does not identify them. Identification may be inferred, however, from the n.m.r. spectra of other olefin coordination compounds of rhodium. In order to consider possible explanations for the absorption difference of the ethylene hydrogen atoms, it is helpful to speculate about the structure of $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$. In a simple valence bond description it may be assumed that, in forming coordination bonds with rhodium, the π -cyclopentadienyl group contributes six electrons and the ethylene molecules two electrons each. Accordingly, Rh(I) ($4s^2$, $4p^6$, $4d^8$) will have acquired 10 electrons and attained the Xe inert gas configuration. The molecule might be pictured (III) as an octahedron with a π -cyclopentadienyl group centered on one face and coordinated at the three apices of that face. Ethylene is bonded at two other corners while an unshared electron pair occupies the sixth apex. On the basis of this geometry two



choices are possible for two sets of four approximately equivalent ethylene protons. The four "upper" protons (H_u of III) might be regarded as comprising one set and the four "lower" protons (H_l of III) as making up the second set. Another choice would make one set of the "inner" four (iH in III) and a second set of the "outer" four (oH in III).¹⁰

A decision between these possibilities can be made on the basis of the n.m.r. spectrum of $\text{AcacRh}(\text{C}_2\text{H}_4)_2$ (Acac = acetylacetonate) (IV). Although at 25° the spectrum of this compound has only one absorption peak



corresponding to ethylenic protons, this peak is split at -5.0° , and the fine structure closely resembles that of $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$. Since the chelated acetylacetonate ligand lies in the coordination plane, H_u and H_l are equivalent and the sets of different protons must be iH and oH . It is inferred that the same differentiation occurs in $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$. This implies that H_u and H_l of $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ (III) have indistinguishable chemical shifts. Possibly the $-\text{C}_5\text{H}_5$ group is symmetrically disposed with respect to coordinated ethylene and III is not a proper description of the structure. It is also possible that the difference in shielding of H_u and H_l is so small that the difference in chemical shifts cannot be detected.

Identification of iH with the high field proton absorption is made from an examination of the n.m.r. spectrum of $\text{C}_5\text{H}_5\text{Rh}(\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}=\text{CH}_2)$ (Fig. 3d). Uncoordinated 1,5-hexadiene has three absorption areas (Fig. 3c). There is a broad absorption at -5.06 to -5.86 p.p.m. with considerable fine structure which is attributed to the vinyl hydrogens on C_2 and C_6 which are split by *cis*- and *trans*-vinyl hydrogens on C_1 and C_6 , respectively, as well as by the methylene protons of C_3 and C_4 . The second group of absorptions extends from -4.40 to -4.80 p.p.m. with four well-defined peaks and corresponds to the four vinyl protons on C_1 and C_6 . The third group, at -1.64 to -1.75 p.p.m., is due to methylene protons on C_3 and C_4 .

On coordination to rhodium in the compound $\text{C}_5\text{H}_5\text{RhC}_6\text{H}_{10}$ (V) the absorptions of the vinyl protons are all shifted upfield. The absorptions of protons on C_2 and C_5 are at -4.83 to -4.30 p.p.m., while the protons on C_1 and C_6 give two well-separated sets. One set, con-

(7) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60**, 836 (1938).

(8) We are indebted to Professor F. A. Cotton for this concept.

(9) F. A. Cotton in J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p. 377.

(10) If it is assumed that $\text{C}_5\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ has C_{2v} symmetry with a bond joining Rh and the center of the C_5H_5 ring as the axis of symmetry, then the two sets of protons will be iH and oH .

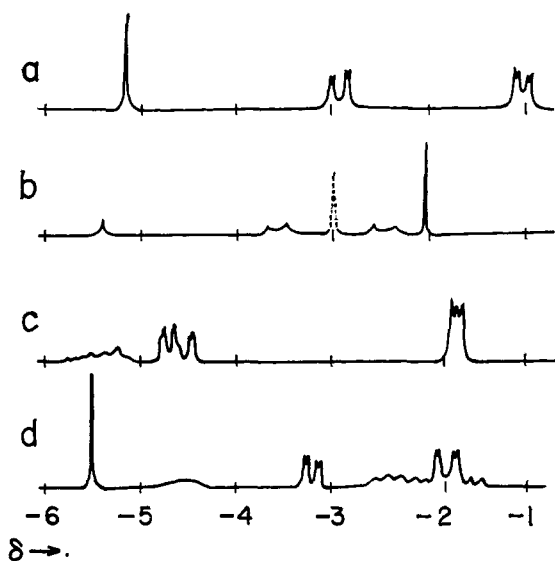
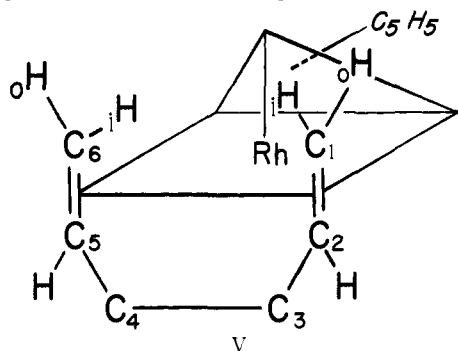


Fig. 3.—Nuclear magnetic resonance spectra of olefin complexes of Rh(I): a, $C_5H_5Rh(C_2H_4)_2$ in $CHCl_3$ at -25° , cyclopentadienyl protons at -5.15 p.p.m., ωH centered at -2.89 p.p.m., iH centered at -1.00 p.p.m.; b, $C_5H_7O_2Rh(C_2H_4)_2$ in $CHCl_3$ at -58° , methylene proton of $C_5H_7O_2$ at -5.38 p.p.m., ωH centered at -3.58 p.p.m., iH centered at -2.51 p.p.m., methyl protons of $C_5H_7O_2$ at -2.03 p.p.m. The peak at -2.96 p.p.m. outlined in a dashed line is due to rotating coordinated ethylene at $+25^\circ$; c, 1,5-hexadiene, neat, protons on C_2 and C_5 at -5.06 to -5.86 p.p.m., protons on C_1 and C_6 at -4.40 to -4.80 p.p.m., protons on C_3 and C_4 at -1.64 to -1.75 p.p.m.; d, $C_5H_5Rh(1,5\text{-hexadiene})$, neat; cyclopentadienyl protons at -5.51 p.p.m., protons on C_2 and C_5 at -4.30 to -4.83 p.p.m., ωH on C_1 and C_6 centered at -3.19 p.p.m., iH on C_1 and C_6 centered at -1.80 p.p.m., protons on C_3 and C_4 at -1.25 to -2.75 p.p.m.

sisting of a pair of doublets centered on -3.13 and -3.26 p.p.m., is identified as the "outside" protons (V) of C_1 and C_6 , because: (1) the splitting of the absorption by the vinyl proton on C_2 or C_5 is relatively small (8.5 c.p.s.) corresponding to a *cis* position to C_2 and C_5 protons¹¹ and (2) the upfield shift on coordina-



tion is relatively small as it is for protons on C_2 and C_5 (which, because of the geometry of the molecule, must be "outside"). The second set of protons on C_1 and C_6 were shifted to -1.72 and -1.91 p.p.m. on coordination. These are believed to be "inside" protons because of relatively large splitting by C_2 - C_5 protons (11 c.p.s.) corresponding to a *trans* position to C_2 and C_5 protons.¹² It is therefore concluded that the protons which are shifted furthest upfield in $AcacRh(C_2H_4)_2$ and $C_5H_5Rh(C_2H_4)_2$ are those that are "inside."

"Long-range shielding"¹² offers a reasonable explana-

(11) 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, p. 193.

(12) (a) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957); (b) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881 (1960); (c) L. M. Jackman,

tion for the absorption difference of "inside" and "outside" ethylene protons and has been discussed in this connection with cycloheptatriene complexes of group VI metals by Bennett, Pratt, and Wilkinson.¹³ They propose that when an uncoordinated olefin is subjected to a strong magnetic field, an anisotropic magnetic field is induced which may be qualitatively represented by a magnetic dipole located at the center of the $C=C$ σ -bond axis and perpendicular to the plane of the carbon and hydrogen atoms. The induced field above and below this plane and within a solid cone which has the dipole as an axis^{12a} opposes the applied magnetic field. The n.m.r. absorption of protons within the cone will be shifted to higher field. When the olefin is coordinated to a metal, this hypothetical magnetic dipole will presumably be shifted toward the metal ion.¹³ It appears that "inside" protons of a coordinated olefin are more strongly shielded than "outside" protons by a second olefin coordinated to the same metal atom.

It is obvious from the marked change under coordination in the chemical shift of terminal methylene groups of 1,5-hexadiene that coordination introduces a strong, unsymmetrical shielding effect. We have made several attempts without success to differentiate by n.m.r. spectra the olefin protons of monoethylene complexes of Fe(II) and Pt(II). Ethylene in $[C_5H_5Fe(CO)_2(C_2H_4)]^+$ ¹⁴ has a single absorption at -5.94 p.p.m. *cis*- $[NH_3(C_2H_4)PtCl_2]$ and *cis*- $[py-(C_2H_4)PtCl_2]$ are so sparingly soluble that their n.m.r. spectra could not be measured. The absorption spectrum of *cis*- $[p-CH_3C_6H_4NH_2(C_2H_4)PtCl_2]$ has a triplet absorption pattern due to ethylene protons. This consists of a central peak at -3.82 p.p.m. which is split by ¹⁹⁵Pt (34% abundance) to give lines ± 32 c.p.s. from the principal absorption.¹⁵ There is no indication in the spectrum of differentiation of the unsymmetrically disposed protons. The reason for failure to distinguish protons in these compounds is uncertain. The $[C_5H_5Fe(CO)_2-(C_2H_4)]^+$ ion may be symmetrical but in *cis*- $[p-CH_3C_6H_4NH_2(C_2H_4)PtCl_2]$ the ethylene protons are certainly in different environments.

Possibly the shielding difference is too small for detection. Alternatively, the rotational barrier may be so low that the protons equilibrate too rapidly for observation.

Ethylene Exchange in Bis-(ethylene)-rhodiumacetylacetonate.—It has been mentioned that there is no exchange between coordinated C_2H_4 in $C_5H_5Rh(C_2H_4)_2$ and C_2D_4 during 5 hr. at 100° . However, exchange between $(Acac)Rh(C_2H_4)_2$ and C_2D_4 is rapid. A chloroform solution of the acetylacetonate to which ethylene is added has a single ethylene absorption at 25° due to both free and coordinated ethylene whose position depends upon the relative amounts of free and coordinated ethylene. Assuming that uncoordinated ethylene protons absorb at -4.9 p.p.m. and coordinated ethylene in $(Acac)Rh(C_2H_4)_2$ absorbs at -3.0 p.p.m., the average lifetime for coordinated ethylene is less than 10^{-4} sec. at 25° .¹⁶ Furthermore, the rate of exchange depends on the concentration of ethylene. At -58° the n.m.r. spectrum of $(Acac)Rh(C_2H_4)_2$ has two well-defined absorptions centered at -3.58 and -2.51 p.p.m. (Fig. 3b) showing that exchange or rotation (if they occur) are too slow to perturb the spectrum. If, however, ethylene is added to the solution of $(Acac)Rh(C_2H_4)_2$ at

"Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 112.

(13) M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2037 (1961).

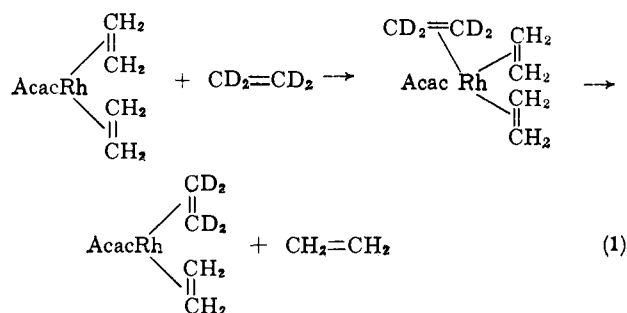
(14) E. O. Fischer and K. Fichtel, *Chem. Ber.*, **94**, 1200 (1961).

(15) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 2519 (1960).

(16) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 64.

—58° there is a single broad absorption at about —3.05 p.p.m. corresponding to a rapid exchange, much faster than ethylene rotation in $C_5H_5Rh(C_2H_4)$ at this temperature. The increased exchange rate upon addition of ethylene suggests a bimolecular reaction.¹⁷

A comparison of the structures of the cyclopentadienyl and acetylacetonate complexes provides a reasonable explanation for the strikingly different behavior of these compounds in exchange of ethylene. As has been mentioned, $C_5H_5Rh(C_2H_4)_2$ may be regarded as having attained rare gas configuration. If it is assumed that the chelated acetylacetonate group contributes four electrons, then Rh(I) in $AcacRh(C_2H_4)_2$ is two electrons short of rare gas configuration and could accommodate two more electrons from an olefin molecule to form an activated complex for an SN_2 exchange reaction (eq. 1). Rhodium in the π - $C_5H_5Rh(C_2H_4)_2$



cannot accommodate a pair of electrons within the fourth electron shell and so does not exchange olefin under the same conditions.

It is interesting to compare the exchange reactions of rhodium carbonyls and olefin complexes. The rate of carbon monoxide exchange with a number of four-coordinate Rh(I) carbonyls has been measured¹⁸ at —80° and, like ethylene exchange in $AcacRh(C_2H_4)_2$, found to be very fast and depend upon the concentration of carbon monoxide. It was expected that, like $C_5H_5Rh(C_2H_4)_2$, $C_5H_5Rh(CO)_2$ ¹⁹ would not exchange bimolecularly with ¹⁴CO and possibly not exchange perceptibly by any mechanism. Exchange of ¹⁴CO and $C_5H_5Rh(CO)_2$ occurs at 0°. Apparently a dissociative mechanism is involved, for the rate does not increase as the concentration of carbon monoxide is raised. Exchange is slower in the dark than in reaction mixtures exposed to indirect sunlight. Ethylene exchange does not take place in illuminated solutions of C_2D_4 and $C_5H_5Rh(C_2H_4)_2$.

Carbon monoxide displaces ethylene from $(C_2H_4)_4Rh_2Cl_2$ and $(Acac)Rh(C_2H_4)_2$ but not from $C_5H_5Rh(C_2H_4)_2$, nor does ethylene displace CO from $C_5H_5Rh(CO)_2$ in 1 hr. at 0°.

Experimental

The olefin coordination compounds of Rh(I) described in the Experimental section are all relatively stable to heat and air. They do not change on storage for months at 10°.

Coordination Compounds.— $(C_2H_4)_4Rh_2Cl_2$ was prepared from rhodium trichloride trihydrate.²⁰ The infrared spectrum (KBr wafer) has absorption at: 3060 (m), 2980 (m), 2020 (w, broad), 1520 (m), 1430 (vs), 1230 (s), 1215 (vs), 999 (vs), 952 (m), 930 (s), 815 (w), 715 (m), 674 (w), and 668 (w) cm^{-1} .

(17) It should be emphasized that although ethylene in $(Acac)Rh(C_2H_4)_2$ is kinetically labile, the complex is thermodynamically stable. Free ethylene is not detected by infrared absorption in the gas phase over a solution of $AcacRh(C_2H_4)_2$ in ethylene glycol heated to 80°.

(18) (a) A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961); (b) A. Wojcicki and H. B. Gray, Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 32M.

(19) E. O. Fischer and K. Bittler, *Z. Naturforsch.*, **16b**, 225 (1961). Material used in experiments reported here was kindly supplied by Dr. G. W. Parshall.

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

$C_5H_5Rh(C_2H_4)_2$ was prepared from cyclopentadienylsodium and $(C_2H_4)_4Rh_2Cl_2$ according to the method of King,⁴ who generously supplied material for use in this work. A KBr wafer of $C_5H_5Rh(C_2H_4)_2$ absorbs at 3415 (w, broad), 3060 (w), 2975 (m), 1880 (w, b), 1740 (w, b), 1635 (w, b), 1580 (w, b), 1493 (w), 1433 (m), 1403 (w), 1196 (s), 1185 (s), 1104 (w), 1010 (m), 987 (w), 965 (m), 906 (w), 847 (w), 818 (w), 787 (s), 723 (m) cm^{-1} .

$(Acac)Rh(C_2H_4)_2$.—A mixture of 3.6 g. (9 mmoles) of $(C_2H_4)_4Rh_2Cl_2$, 50 ml. of ethyl ether, and 1.8 ml. (18 mmoles) of acetylacetonate was chilled to —80° and a solution of 3 g. of potassium hydroxide in 10 ml. of water was added dropwise. The mixture was warmed to 0° with shaking, and 50 ml. more of ether was added. This mixture was stirred at 0° for 0.5 hr. The ether layer was separated, filtered, and chilled to —80°. The orange-yellow platelets that crystallized weighed 3.8 g. By concentration of the filtrate and cooling again to —80°, 0.5 g. more of the acetylacetonate was isolated, m.p. 144–146°. A KBr wafer has the following absorption pattern: 3415 (m), 3060 (w), 2985 (w), 1575 (s), 1558 (s), 1524 (s), 1425 (m), 1372 (m), 1361 (m), 1267 (m), 1233 (m), 1221 (w), 1199 (w), 1029 (m), 1015 (w), 987 (w), 936 (m), 788 (m), 784 (w) cm^{-1} .

Anal. Calcd. for $C_9H_{15}O_2Rh$: C, 41.88; H, 5.86. Found: C, 42.08; H, 5.98.

$(CH_2=CHCH_2CH_2CH=CH_2)RhCl$.—A suspension of 4 g. (10 mmoles) of $(C_2H_4)_4Rh_2Cl_2$ in 20 ml. of diethyl ether was treated at room temperature with 2.4 ml. of 1,5-hexadiene (20 mmoles). Ethylene was vigorously and completely evolved within 3 min. The product which crystallized from the reaction mixture weighed 4.2 g. It was recrystallized by cooling to —80° a toluene solution saturated at 25°; m.p. 115–117° dec. A KBr wafer of $C_{12}H_{20}Rh_2Cl_2$ absorbs at 3040 (w), 2980 (w), 2910 (m), 2860 (m), 2030 (w), 1900 (w), 1490 (s), 1450 (m), 1430 (vs), 1385 (m), 1340 (w), 1300 (s), 1235 (s), 1230 (m), 1200 (m), 1180 (m), 1105 (s), 1060 (w), 1005 (w), 1000 (w), 984 (w), 963 (vs), 954 (w), 935 (m), 924 (s), 915 (vs), 850 (vs), 830 (w), 760 (m) cm^{-1} .

Anal. Calcd. for $C_{12}H_{20}Rh_2Cl_2$: C, 32.69; H, 4.57; Cl, 16.07; mol. wt., 441. Found: C, 32.31; H, 4.61; Cl, 16.35; mol. wt., 482 (cryoscopic, in benzene).

$CH_2=CHCH_2CH_2CH=CH_2RhC_5H_5$.—To 12 ml. of a 1.8 M solution of cyclopentadienylsodium (22 mmoles) in tetrahydrofuran was added 4.2 g. (9.6 mmoles) of $(CH_2=CHCH_2CH_2CH=CH_2)RhCl$. The solution was stirred at about 25° for 2 hr. in a nitrogen atmosphere. Solvent was removed at 25° (0.2 mm.) and the residue was distilled using a short path still at a pressure of 0.1 mm. and a pot temperature of 100°. The product was an orange-red liquid which freezes at 10°.

Anal. Calcd. for $C_{11}H_{13}Rh$: C, 55.01; H, 6.30; mol. wt., 240. Found: C, 54.12; H, 6.45; mol. wt., 235 (cryoscopic, in benzene).

A film of the liquid absorbs infrared radiation at 3920 (w), 3070 (vs), 2990 (vs), 2930 (vs), 2880 (vs), 2830 (vs), 1875 (w), 1785 (w), 1730 (w), 1670 (w), 1630 (w), 1550 (w), 1485 (vs), 1460 (w), 1440 (s), 1405 (s), 1380 (s), 1350 (m), 1330 (s), 1300 (m), 1230 (vs), 1195 (s), 1180 (s), 1105 (vs), 1050 (w), 1010 (vs), 995 (vs), 947 (s), 929 (s), 912 (s), 893 (w), 843 (vs), 830 (m), 784 (vs) cm^{-1} .

$[C_5H_5Fe(CO)_2C_2H_4]^+$ was prepared from $C_5H_5Fe(CO)_2I$ by the method of Fisher and Fichtel.¹⁴ A glass cylinder with labyrinth inlet was charged with 0.6 g. (2 mmoles) of $C_5H_5Fe(CO)_2I$, 10 ml. of benzene, and 1.1 g. (4 mmoles) of $AlBr_3$. The cylinder was placed in a shaking autoclave, and the reaction mixture subjected to ethylene at 30° and 1300–1600 p.s.i. for 16 hr. The pressure dropped 300 p.s.i. during the first 30 min. The reaction mixture was treated with 50 ml. of anhydrous ether, chilled to —10°, and D_2O was added dropwise until an aqueous phase of about 1 ml. had accumulated. The nearly colorless ether-benzene phase was decanted, and the deep brown D_2O solution centrifuged. A portion of this hydrolysate was examined using a Varian A-60 n.m.r. spectrometer. There were three absorption bands located at —4.11, —6.08, and —6.47 p.p.m. Absorption at —6.47 p.p.m. is due to HD_2O^+ since addition of a small amount of water shifted this peak to —5.94 p.p.m. The peak at —4.11 p.p.m. is attributed to π -cyclopentadienyl protons since $C_5H_5Fe(CO)_2I$ absorbs at —4.08 p.p.m. The peak at —6.08 p.p.m. is ascribed to coordinated ethylene.

cis- $[(p-CH_3C_6H_4NH_2)Pt(C_2H_4)_2Cl_2]$.—A solution of 10 g. (24 mmoles) of K_2PtCl_4 and 4.5 g. (45 mmoles) of $p-CH_3C_6H_4NH_2$ in 150 ml. of water precipitated $[(p-CH_3C_6H_4NH_2)_2PtCl_2]$ on standing for 16 hr. This compound was separated by centrifuge and heated under reflux with 150 ml. of 1 M aqueous HCl to prepare $[p-CH_3C_6H_4NH_3]^+ [(p-CH_3C_6H_4NH_2)PtCl_2]^-$. Dissolution was nearly complete after 80 hr. The solution was filtered and shaken with ethylene at 25° and 40 p.s.i. pressure for 16 hr. Pale yellow *cis*- $[(p-CH_3C_6H_4NH_2)Pt(C_2H_4)_2Cl_2]$ separated; yield 2.4 g. (6 mmoles).

Anal. Calcd. for $C_9H_{13}PtCl_2N_2$: C, 26.93; H, 3.27; Cl, 17.68. Found: C, 27.30; H, 3.56; Cl, 16.99.

The n.m.r. proton spectrum of a CD_3COCD_3 solution of *cis*-[(*p*- $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$) $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2$] had a pair of narrowly separated peaks at -6.84 p.p.m. (phenyl protons) and a broad peak centered at about -6.30 p.p.m. (amine proton). A peak at -3.81 p.p.m. with smaller peaks ± 32 c.p.s. from it is ascribed to coordinated ethylene split by ^{195}Pt ; the combined area under the smaller peaks is 33% of the total absorption ascribed to ethylene protons. A peak at -1.87 p.p.m. is due to methyl protons. The location and form of the absorption due to coordinated ethylene are not perceptibly different at -60° .

$\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{D}_4)_2$.—A heavy-walled, 75-ml. glass tube was charged with a solution of 0.8 g. of "rhodium trichloride trihydrate" in 1.6 ml. of water, 30 ml. of methanol, and 300 ml. of C_2D_4 . The sealed tube was stored at 0° for 48 hr. and 0.3 g. of $[(\text{C}_2\text{D}_4)_2\text{RhCl}]_2$ recovered by filtration.

The sample $[(\text{C}_2\text{D}_4)_2\text{RhCl}]_2$ was stirred with 2 ml. of a 1.8 M solution of $\text{C}_3\text{H}_5\text{Na}$ in tetrahydrofuran for 2 hr. at 25° . The reaction mixture was concentrated under vacuum and the product sublimed at a pressure of about 0.2 mm. and a bath temperature of 50° . The yield of $\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{D}_4)_2$ was 0.2 g.

Rotation Rate Measurements on $\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$.—Rates were measured using a Varian Associates spectrometer (HR 60). Temperatures were adjusted with a Varian Model V-4340 variable temperature probe accessory.

Chloroform Medium.—A solution prepared from 0.30 ml. of CDCl_3 and 0.15 g. of $\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ was pipetted into a 4×24 mm. n.m.r. tube. The air over the solution was displaced with ethylene, the tube was sealed, and the n.m.r. spectrum measured at intervals over the range -20 to 60° . The positions of the absorption maxima of the two kinds of ethylene proton were measured by side-band modulation of the chloroform proton absorption. The results are summarized in Table I and from them values for E_a and ν_0 were calculated as described earlier.

Toluene Medium.—The test solution of 0.30 ml. of $\text{C}_6\text{H}_5\text{CH}_3$ and 0.15 g. of $\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ was prepared as described for the experiment in CDCl_3 , and the spectrum was measured over the same temperature interval.

The results of the experiment are

Temp., °C.	$\delta\omega_e$, cycles sec. ⁻¹	$1/\tau\delta\omega^a$	$1/T \times 10^3$
-28	110		
27	106	0.20	3.33
30	106	.20	3.30
34	103	.25	3.26
39	97	.33	3.21
43	95	.36	3.16
46	85	.45	3.13
50	76	.51	3.10

$$^a 1/\tau\delta\omega = [1/2(1 - \delta\omega_e^2/\delta\omega^2)]^{1/2}$$

From a plot of $1/\tau\delta\omega$ against $1/T \times 10^3$, values of E_a and ν_0 were calculated as described earlier. The results are given in Table II.

***d*₈-Acetone Medium.**—A solution of 0.10 g. of $\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ in 0.30 ml. of CD_3COCD_3 was prepared as described for the experiment in CDCl_3 and the n.m.r. spectrum was measured over the same temperature interval. The results of the experiment are

Temp. °C.	$\delta\omega_e$, cycles sec. ⁻¹	$1/\tau\delta\omega^a$	$1/T \times 10^3$
-19	116 ^b		
20	115	0.1	3.45
27	109	.25	3.33
33.5	106	.28	3.26
37.5	103	.33	3.22
41	103	.33	3.18
43	94	.40	3.16
49	91	.44	3.11
52	83	.50	3.08

^a $1/\tau\delta\omega = [1/2(1 - \delta\omega_e^2/\delta\omega^2)]^{1/2}$. ^b Used for $\delta\omega$ in calculation of $1/\tau\delta\omega$. E_a and ν_0 , calculated from the plot of $1/\tau\delta\omega$ against $1/T$, are given in Table II.

Effect of $\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ Concentration on Exchange Rate.—At -3° , the rate of isomerization of ethylene protons in a 30% solution of $\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ in CHCl_3 is slow enough that splitting of an absorption due to a proton on C_1 by a *trans* proton on C_2 is barely perceptible. If exchange were a bimolecular reaction, dilution would slow down the reaction and give better definition of this splitting. However, solutions containing 15, 7.5, and 4% $\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ gave equally diffuse spectra at -3° and in these solutions the rates of a bimolecular reaction would be reduced to approximately 1/4, 1/16, and 1/64, respectively, of the rate in the original solution.

N.m.r. Spectra of (Acac)Rh(C₂H₄)₂-Ethylene Mixtures.—A solution of 0.02 g. of (Acac)Rh(C₂H₄)₂ in 0.5 ml. of CHCl_3 had an n.m.r. spectrum at -58° with absorptions at -3.69 , -3.47 , -2.63 , and -2.39 p.p.m. due to the ethylene protons ("inside" and "outside" protons split by the *trans*-proton on the other ethylene C-atom). A similar solution containing 12 ml. of gaseous C_2H_4 had a very broad absorption at -58° covering a range of >0.8 p.p.m. and centered on -2.96 p.p.m.

A series of solutions of 0.05 g. of (Acac)Rh(C₂H₄)₂ in 0.4 ml. of CHCl_3 containing 4, 8, and 24 ml. of gaseous C_2H_4 (coordinated C_2H_4 /free $\text{C}_2\text{H}_4 = 2.4, 1.2, \text{ and } 0.4$, respectively) had single, moderately broad (0.25 p.p.m.) absorptions due to ethylene protons located at -3.50 , -3.91 , and -4.52 p.p.m., respectively. The shift toward a lower field corresponds to the increasing contribution of free C_2H_4 (-4.95 p.p.m.) to the average environment of the ethylene protons.

Exchange Reactions. CH_3OD with $\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$.—A solution of 0.02 g. of $\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ (0.8 mmole) in 2 ml. of CH_3OD (50 mmoles) was held at 25° for 4 hr., then chilled to -80° to crystallize the $\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$. CH_3OD was removed by pipet, and the crystals were dried under vacuum at 25° . The dried $\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ was dissolved in 0.5 ml. of C_6H_6 . The integrated n.m.r. spectrum of the solution (Varian Associates A-60 n.m.r. spectrometer) showed that the ratio H(cyclopentadienyl)/H(ethylene) was 5/7.5. With the relative amounts of $\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ and CH_3OD used, equilibration should have given essentially complete deuteration of ethylene so it is concluded no exchange occurred.

C_2D_4 with $\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$.—A solution of 0.05 g. (0.2 mmole) of $\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ in 0.4 ml. of methanol and 15 ml. (0.5 mmole) of gaseous C_2D_4 were sealed in a 4×24 mm. n.m.r. tube. After 7 days at 25° followed by 5 hr. at 50° and 5 hr. at 100° , the n.m.r. spectrum recorded on a Varian A-60 n.m.r. spectrometer showed no evidence of absorption due to free C_2H_4 . The infrared spectrum of the gas recovered from the tube showed no absorption due to C_2H_4 .

Similar experiments were made with chloroform, ethanol, and acetone as solvents. There was no exchange in CHCl_3 after 2 days at 25° and no exchange in ethanol during 8 days at 25° . In acetone after 2.5 days at 25° a weak absorption attributed to C_2H_4 (-4.94 p.p.m.) and corresponding to less than 5% of the coordinated ethylene had appeared but, since some solid had precipitated from the initially clear solution, a reaction other than simple exchange may have occurred.

^{14}CO with $\text{C}_3\text{H}_5\text{Rh}(\text{CO})_2$.—A 7-mg. sample of ^{14}CO obtained from New England Nuclear Corp. was described as containing 0.5 curie of ^{14}CO . It was diluted to 1 l. with ordinary CO , giving a gas mixture which had a calculated disintegration rate of 1.1×10^6 ml.⁻¹ min.⁻¹. Flasks with a capacity of 25 ml. were charged with 5 ml. of a solution of 0.1 g. of $\text{C}_3\text{H}_5\text{Rh}(\text{CO})_2$ in 100 ml. of toluene, chilled in liquid nitrogen, and evacuated. A measured amount of C^*O was added from a gas buret and the flasks immersed in an ice-water bath while the contents were agitated by a magnetic stirrer. Some mixtures were protected from light while others were exposed to normal laboratory illumination. After 5 hr. the flasks were chilled to -80° and evacuated by an oil pump. Radioactivity was measured by scintillation counting.

Charged, ml. C^*O	Illumination	Counts/ml./min.
20	Dark	6,000
10	Dark	12,000
20	Exposed	159,000
10	Exposed	138,000

Displacement of Coordinated Ethylene by CO .—The infrared cell used in the following experiments was equipped with a small side arm and had NaCl windows. The path length was 10 cm. and the volume was 40 ml. The side arm was charged with 0.03 g. (0.12 mmole) of (Acac)Rh(C₂H₄)₂ and 1 ml. of ethylene glycol. The cell was evacuated and 5 ml. of CO was introduced. The suspended olefin complex dissolved within a few minutes and the infrared spectrum of the gas in the cell showed the characteristic absorption pattern of ethylene. $(\text{C}_2\text{H}_4)_2\text{Rh}_2\text{Cl}_2$ reacted with CO in a similar manner but no detectable amount of ethylene was displaced from $\text{C}_3\text{H}_5\text{Rh}(\text{C}_2\text{H}_4)_2$ in 7 days at 25° .

Attempted Displacement of CO in $\text{C}_3\text{H}_5\text{Rh}(\text{CO})_2$ by C_2H_4 .—A solution of 0.2 g. of $\text{C}_3\text{H}_5\text{Rh}(\text{CO})_2$ (ca. 1 mmole) in 10 ml. of ether was stirred with 25 ml. of ethylene at 0° for 1 hr. The solution was chilled to -40° and a gas sample withdrawn for infrared examination. There was no absorption attributable to CO .

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