Two significant differences between these similar classes of compounds are (a) the barrier to internal rotation for the π-C_5H_5 group is low whereas the barrier to internal rotation for the tris(1-pyrazolyl)borate ligand about the Mo–B axis is quite high (see above); (b) in the case of the π-$C_5H_5Mo(CO)_2LR$ two isomers can be observed corresponding to cis and trans positions for the ligands L and R. In the present case the π-$CH_2C(R_2)CH_2^-$ ligand can occupy only two cis positions. The cis and trans isomers of the complexes π-$C_5H_5Mo(CO)_2LR$ can interconvert through an intramolecular process with a trans → cis barrier which varies between 12 and 26 kcal/mol^{-1} depending mainly on the nature of the ligand R.

Faller and Anderson[12] discuss this rearrangement process in terms of a pseudo-five-coordinate model for the complexes. The lowest energy configuration is considered to be approximately square pyramidal with the π-C_5H_5 ligand located at the apex and the four other ligands located at the base. The cis and trans isomers can then interconvert *via* a "trigonal-bipyramidal" intermediate with the π-C_5H_5 ligand in an axial position.

In the case of the tris(1-pyrazolyl)borate–molybdenum complexes, a process of the type described by Faller and Anderson[12] can exchange the two CO ligands or can exchange the two ends of the π-$CH_2C(R_2)CH_2^-$ ligand. However, the three bridging pyrazolyl groups cannot become equivalent on the nmr time scale unless internal rotation about the Mo–B axis occurs at some stage. It is quite possible that a combination of the two processes is taking place.

Olefin Coordination Compounds of Rhodium. VI. Dissociative Displacement of Ethylene from Rhodium(I) and the Strength of the Rh–C_2H_4 Bond in π-$C_5H_5Rh(C_2H_4)_2$

Richard Cramer

Contribution No. 1877 from the Central Research Department,
Experimental Station, E. I. du Pont de Nemours and Company,
Wilmington, Delaware 19898.
Received November 15, 1971

Abstract: Ethylene can be cleanly displaced from π-$C_5H_5Rh(C_2H_4)_2$ by various nucleophiles through a mechanism whose rate-determining step is dissociative loss of C_2H_4. A study of the gas-phase pyrolysis of π-$C_5H_5Rh(C_2H_4)_2$ indicates a maximum value of about 31 kcal for the strength of the Rh–C_2H_4 bond in that compound.

Displacement of ethylene from acac$Rh(C_2H_4)_2$ by nucleophiles (CO, CN^-, phosphines, amines, etc.) is a very fast reaction. For example, the exchange rate of coordinated ethylene is $>10^4$ sec^{-1} at 25°.[1] This exchange occurs through the familiar bimolecular substitution mechanism of d^8 square-planar molecules;[2] ethylene is the attacking nucleophile. On the other hand, ethylene in π-$C_5H_5Rh(C_2H_4)_2$ is not easily displaced by nucleophiles[1,3] and this behavior is consistent with bimolecular substitution theory.[2] In acac$Rh(C_2H_4)_2$, Rh has the electronic structure [Kr] $5s^24d^{10}5p^4$ which is two electrons short of rare gas configuration. With a small increase in energy, Rh(I) can accommodate two electrons of an entering ligand (thus attaining rare gas configuration) to form a five-coordinate intermediate for an SN2 displacement. However, assuming C_5H_5 donates six electrons, Rh in π-$C_5H_5Rh(C_2H_4)_2$ is [Kr] $5s^24d^{10}5p^6$, and an SN2 reaction is inhibited because the electrons of the entering nucleophile would have to be promoted into a high-energy orbital.

Ethylene in π-$C_5H_5Rh(C_2H_4)_2$ is readily displaced in a bimolecular reaction by electrophiles. The Rh atom can be considered to have an unshared pair of d^2sp^3 electrons and thus add a Lewis acid to form the requisite intermediate.[4]

The inertness of π-$C_5H_5Rh(C_2H_4)_2$ to SN2 attack by nucleophiles provides the opportunity for study of ligand displacement by a third mechanism, *viz.*, dissociation of an ethylene ligand (eq 1 and 2). We have

$$\pi\text{-}C_5H_5Rh(C_2H_4)_2 \longrightarrow \pi\text{-}C_5H_5Rh(C_2H_4) + C_2H_4 \quad (1)$$

$$\pi\text{-}C_5H_5Rh(C_2H_4) + L \longrightarrow \pi\text{-}C_5H_5Rh(C_2H_4)L \quad (2)$$

found that this mechanism becomes available above about 115°, and by studying the kinetics of reaction 1 in the gas phase we have tentatively evaluated the strength of the rhodium–ethylene bond in π-$C_5H_5Rh(C_2H_4)_2$.

Dissociative Displacement in Solution

Displacement of ethylene from π-$C_5H_5Rh(C_2H_4)_2$ by a nucleophile was demonstrated by heating a solution of 0.070 mmol of π-$C_5H_5Rh(C_2H_4)_2$ and 1.0 mmol of 1,5-cyclooctadiene in 5 ml of diphenyl ether at 136°. Ethylene was evolved (0.126 mmol after 1 hr) and after 1.5 hr π-C_5H_5Rh(1,5-COD) was recovered (>90% conversion).

In order to substantiate the mechanism of this reaction we studied the kinetics of ethylene displacement from π-$C_5H_5Rh(C_2H_4)_2$ by various ligands. If the

---

[1] R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964).

[2] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 375.

[3] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, **10**, 1165 (1971).

[4] R. Cramer, *J. Amer. Chem. Soc.*, **89**, 5377 (1967).

rate-determining step were dissociation of ethylene from π-$C_5H_5Rh(C_2H_4)_2$, we would expect, first, that the rate of ethylene displacement would be independent of the concentration of the entering nucleophile. Second, as the following analysis suggests, the rate may vary with the displacing ligand but the fastest rate should be no larger than twice the slowest. The reactions to be considered are shown in eq 3–6. Experiments will be

$$\pi\text{-}C_5H_5Rh(C_2H_4)_2 \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \pi\text{-}C_5H_5Rh(C_2H_4) + C_2H_4 \tag{3}$$

$$\pi\text{-}C_5H_5Rh(C_2H_4) + L \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} \pi\text{-}C_5H_5Rh(C_2H_4)L \tag{4}$$

$$\pi\text{-}C_5H_5Rh(C_2H_4)L \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} \pi\text{-}C_5H_5RhL + C_2H_4 \tag{5}$$

$$\pi\text{-}C_5H_5RhL + L \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} \pi\text{-}C_5H_5RhL_2 \tag{6}$$

described later to show that in the gas phase eq 3 is reversed at low ethylene pressure. This implies that equilibrium in eq 3 lies to the left and that $k_{-3} > k_3$. We assume that k_{-3}, k_4, k_{-5}, and k_6 are all greater than k_3 k_{-4}, k_5, and k_{-6}. Further, all the reaction systems under consideration here lead, ultimately, to displacement of both ethylene ligands by nucleophile. Consequently the rate of ethylene liberation is $k_3[\pi\text{-}C_5H_5Rh(C_2H_4)_2] + k_5[\pi\text{-}C_5H_5Rh(C_2H_4)L]$. If k_5 is very small (*i.e.*, if L tends to stabilize π-$C_5H_5Rh(C_2H_4)L$ against loss of ethylene), π-$C_5H_5Rh(C_2H_4)L$ will accumulate and the rate of ethylene evolution will approximate $k_3[\pi\text{-}C_5H_5Rh(C_2H_4)_2]$. On the other hand if k_5 is very large (*i.e.*, if L destabilizes π-$C_5H_5Rh(C_2H_4)L$ so that it loses ethylene readily), π-$C_5H_5Rh(C_2H_4)L$ will react as fast as it is formed and the rate of ethylene evolution will be $2k_3[\pi\text{-}C_5H_5Rh(C_2H_4)_2]$. These two conditions set the limits for the rate of ethylene liberation. Examples of both types of L will be described later.

The rate of ethylene displacement was followed by infrared spectrophotometry; details are given in the Experimental Section. Typical results covering phosphines, pyridines, olefins, and a nitrile as nucleophiles are summarized in Table I. The rates were calculated by plotting moles of C_2H_4 released against time. A tangent was drawn to the smooth plot at zero time and the slope of that tangent divided by the moles of π-$C_5H_5Rh(C_2H_4)_2$ charged gives k. These rate constants are consistent with a rate-determining dissociation of ethylene. Specifically, the rate did not change when the concentration of the nucleophile Ph_3P was increased sixfold (expt 1 and 2). Also the values of k_4 for reaction at 118° lie within the limits of 1.65×10^{-4} (with Ph_3P, expt 2) and 3.48×10^{-4} sec^{-1} (with 1,5-COD, expt 11); a ratio of 1/2.1 compared with an expected minimum ratio of 1/2. The range of values for k reflects the extent to which eq 5 contributes to release of ethylene.

Our interpretation of the data of Table I is that in displacement of ethylene by 1,5-COD, release of the second ethylene ligand is fast, *i.e.*, $k_5 > k_3$. Accordingly, the results of experiments 10–13 can be used to calculate an activation energy for eq 3 of $E_A \approx 29$ kcal. When π-$C_5H_5Rh(C_2H_4)_2$ is heated to 136° in diphenyl ether (with no displacing ligand other than solvent), over 90% of the ethylene is released and a dark, but apparently homogeneous reaction solution results. Recent results of Schrock and Osborn[5] indicate that diphenyl ether could coordinate with π-$C_5H_5Rh(C_2H_4)$. Possibly a diphenyl ether complex is an ubiquitous intermediate in this dissociative displacement of ethylene, playing a role similar to that of water in substitution reactions of octahedral complexes.[6] There are several reasons for believing that diphenyl ether, if it does coordinate with rhodium, forms a substantially weaker bond than the other ligands under consideration here. One reason is that acac$Rh(C_2H_4)_2$ dissolved in diphenyl ether evolves ethylene about as slowly ($k = 0.95 \times 10^{-4}$ sec^{-1} at 118.2°) as π-$C_5H_5Rh(C_2H_4)_2$ showing that diphenyl ether does not coordinate strongly enough to acac$Rh(C_2H_4)_2$ to promote SN2 displacement of ethylene. Second, the rate of ethylene release from π-$C_5H_5Rh(C_2H_4)_2$ is substantially slower in the absence of added nucleophile (*cf.* expt 14 and 2). This is attributed to recombination of ethylene and π-$C_5H_5Rh(C_2H_4)$ so if diphenyl ether coordinates to Rh it is displaced more easily than other nucleophiles by ethylene. A consideration of the details of dissociative exchange raises problems similar to those encountered in the solvolytic reaction of carbon compounds.[7] Accordingly, in order to get a less complicated value for the energy required to break the Rh–C_2H_4 bond, the reaction was studied in the gas phase.

Table I. Rate of Displacement of C_2H_4 from π-$C_5H_5Rh(C_2H_4)_2$ by Nucleophiles

Expt	π-C_5H_5Rh-$(C_2H_4)_2$, mmol	Nucleophile (mmol)	Temp, °C	$k \times 10^4$ sec^{-1}
1	0.094	Ph_3P (1.23)	118.2	1.73
2	0.090	Ph_3P (0.20)	118.2	1.65
3	0.095	$Ph_2PCH_2CH_2PPh_2$ (0.62)	118.2	2.80
4	0.100	*p*-Ph-pyridine (1.23)	118.2	2.45
5	0.092	Dipy (1.27)	118.2	1.90
6	0.089	*p*-CH_3PhCN (1.23)	118.2	2.15
7[a]	0.100	*p*-CH_3PhCN (1.23)	118.2	2.52
8	0.091	$PhCH_2CH{=}CH_2$ (0.73)	118.2	1.70
9	0.094	Diethyl fumarate (1.23)	118.2	2.93
10	0.107	1,5-COD (0.62)	118.2	3.45
11	0.117	1,5-COD (0.62)	118.2	3.48
12	0.077	1,5-COD (0.62)	136.2	17.0
13	0.069	1,5-COD (0.62)	136.2	19.0
14	0.0915	None	118.2	0.81
15	0.0820	None	136.2	7.25
16	0.091	C_2H_4 (0.1)	118.2	0.70

[a] Run in 6.0 ml of bis(2-hydroxyethyl) ether; in all the other experiments the solvent was diphenyl ether.

Before describing that work, some experiments will be reported which indicate the effect of L on the stability of the Rh–C_2H_4 bond of π-$C_5H_5Rh(C_2H_4)L$. The proton nmr spectrum of π-$C_5H_5Rh(C_2H_4)_2$ has absorptions in three regions. π-C_5H_5 protons account for a sharp downfield (δ 5.15 ppm) singlet. Hydrogen of coordinated ethylene is responsible for two upfield

---

(5) R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, **93**, 3089 (1971).

(6) Reference 2, pp 129–138.

(7) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, pp 151–160.

Table II. Gas-Phase Pyrolysis of $\pi\text{-}C_5H_5Rh(C_2H_4)_2$

Run no.	Reaction temp, °C	Pressure, mm	π-CpRhE$_2$ sublimed, mmol	Unreacted π-CpRhE$_2$, mmol	C_2H_4, mmol/2	π-CpRhE$_2$ lost, mmol	Flow, ml/sec	Reactor volume, ml	k, sec^{-1}	Remarks
1	260	10	0.166	0.010	0.140	0.016	55	30	4.95	
2	261	10	0.139	0.007	0.125	0.007	55	30	5.37	
3	261	10	0.187	0.166		0.021	73	30		Ethylene carrier gas
4	238	10	0.179	0.061	0.102	0.016	53	30	1.74	
5	234	10	0.223	0.064		0.158	75	30		Ethane carrier gas
6	202	20	0.073	0.054	0.015	0.004	24.1	30	0.196	
7	205	20	0.125	0.072	0.026	0.027	24.6	30	0.252	
8	212	10	0.262	0.062	0.187	0.013	47	235	0.278	Large tube
9	203	10	0.243	0.114	0.109	0.020	47.1	195	0.162	Packed large tube

absorptions (centered at 2.89 and 1.00 ppm). At 25° these upfield absorptions are broad and featureless because the protons exchange positions at a rate comparable with the nmr time scale[1] but below 0° this motion is frozen out and the absorptions have a characteristic complex form.

A solution of 0.25 mmol of $\pi\text{-}C_5H_5Rh(C_2H_4)_2$ and 1 mmol of Ph_3P in 0.7 ml of C_6D_6 has the characteristic spectrum of $\pi\text{-}C_5H_5Rh(C_2H_4)_2$ with absorptions of Ph_3P superimposed. If the tube is sealed and the solution is heated at 100° for 1 hr, the spectrum does not change detectably. But if the specimen is heated at 130° for 1 hr, a number of changes are noted which are consistent with the reaction shown in eq 7. (1) The

$$\pi\text{-}C_5H_5Rh(C_2H_4)_2 + Ph_3P \longrightarrow \pi\text{-}C_5H_5Rh(C_2H_4)(PPh_3) + C_2H_4 \qquad (7)$$

peak due to cyclopentadienyl protons of $\pi\text{-}C_5H_5Rh(C_2H_4)_2$ fades and is largely replaced by a new one 0.20 ppm further downfield which is attributed to cyclopentadienyl protons of $\pi\text{-}C_5H_5Rh(C_2H_4)(PPh_3)$. (2) A second singlet in this region results from displaced ethylene. (3) The peaks due to coordinated ethylene have about half their initial intensity and the upper one is shifted downfield about 0.10 ppm. Also, these peaks now have the characteristic complex structure which indicates hindered rotation of ethylene in $\pi\text{-}C_5H_5Rh(C_2H_4)(PPh_3)$. Integration of the spectrum suggested that about 94% of the $\pi\text{-}C_5H_5Rh(C_2H_4)_2$ was converted to $\pi\text{-}C_5H_5Rh(C_2H_4)(PPh_3)$.

A similar result is obtained from 0.25 mmol of $\pi\text{-}C_5H_5Rh(C_2H_4)_2$ in 0.7 ml of CD_3SOCD_3. After 1 hr at 130° the nmr spectrum corresponds to about 80% conversion of $\pi\text{-}C_5H_5Rh(C_2H_4)_2$ to $\pi\text{-}C_5H_5Rh(C_2H_4)(CD_3SOCD_3)$. Again the rotation of the coordinated ethylene is frozen out, and in this compound the location of coordinated ethylene absorptions is considerably changed, *viz.*, δ 2.57 and 1.57 ppm. Thus, when L is Ph_3P or CD_3SOCD_3, $\pi\text{-}C_5H_5Rh(C_2H_4)L$ can be isolated and is stable relative to $\pi\text{-}C_5H_5Rh(C_2H_4)_2$.

On the other hand 0.25 mmol of $\pi\text{-}C_5H_5Rh(C_2H_4)_2$ and 1 mmol of maleic anhydride in 0.5 ml of CD_3COCD_3 are completely converted to $\pi\text{-}C_5H_5Rh(C_4H_2O_3)_2$ after 1 hr at 130° and, as noted earlier, $\pi\text{-}C_5H_5Rh(C_2H_4)_2$ and 1,5-COD yield $\pi\text{-}C_5H_5Rh(1,5\text{-}COD)$.

Gas-Phase Pyrolysis of $\pi\text{-}C_5H_5Rh(C_2H_4)_2$

$\pi\text{-}C_5H_5Rh(C_2H_4)_2$ is sufficiently volatile at 80–85° to be picked up at the rate of 0.1–0.2 mmol hr^{-1} by a carrier gas supplied at a pressure of 10–20 mm and a flow rate of 25 ml min^{-1} (STP) (corresponds to about 25–75 ml sec^{-1} under reaction conditions). At temperatures between 200 and 260° and a contact time of $\approx$0.5 sec, between 25 and 95% of the $\pi\text{-}C_5H_5Rh(C_2H_4)_2$ decomposed to C_2H_4 and other products. Rhodium was deposited as a mirror in the heated zone of the pyrolysis tube and (unidentified) products from C_5H_5 collected on the walls of the reactor just beyond the heated zone. About 90–95% of the $\pi\text{-}C_5H_5Rh(C_2H_4)_2$ that was pyrolyzed was accounted for either as C_2H_4 or as unchanged $\pi\text{-}C_5H_5Rh(C_2H_4)_2$.

In order to facilitate analysis (see Experimental Section) carbon dioxide was employed as carrier gas. The pyrolysis mixture contained about 99.7 mol % CO_2 and 0.3 mol % $\pi\text{-}C_5H_5Rh(C_2H_4)_2$ (or decomposition products) so it is assumed to have flow characteristics of CO_2, *i.e.*, laminar flow (Reynolds no. ~5.2).

A problem frequently encountered in flow system kinetics is uncertainty about the time the substrate spends in the hot zone. This arises from channeling (nonhomogeneous flow) of the gas stream.[8] To avoid errors resulting from channeling, the pyrolysis tube had the same diameter and was colinear with the flask in which CO_2 was saturated with $\pi\text{-}C_5H_5Rh(C_2H_4)_2$. As a further precaution, check experiments were run in a tube whose diameter was three times as large as usual—in some cases empty, in others packed with glass rings. Operation with a carrier gas and a rhodium-covered pyrolysis tube (conditions which were imposed by our reaction system) has been described[9] as advantageous for the study of gas-phase thermolyses.

Rates were calculated using the equation

$$k = v/a \ln C_0/C \qquad (8)$$

where v = gas velocity (ml sec^{-1}), a = reactor volume (ml), C_0 = initial concentration of reactant, C = final concentration of reactant. This equation is appropriate for a plug-flow system with no backmixing.[10] Experimental results are summarized in Table II.

One of the most significant experiments is no. 3 of Table II. In this experiment ethylene was used as the carrier gas instead of carbon dioxide and as a consequence $\pi\text{-}C_5H_5Rh(C_2H_4)_2$ was markedly stabilized.

---

[8] J. J. Batten, *Aust. J. Appl. Sci.*, **12**, 11 (1961).

[9] H. Kwart, S. F. Sarner, and J. H. Olson, *J. Phys. Chem.*, **73**, 4056 (1969).

[10] H. Melville and B. G. Gowenlock, "Experimental Methods in Gas Reactions," Macmillan, New York, N. Y., 1964, p 364.

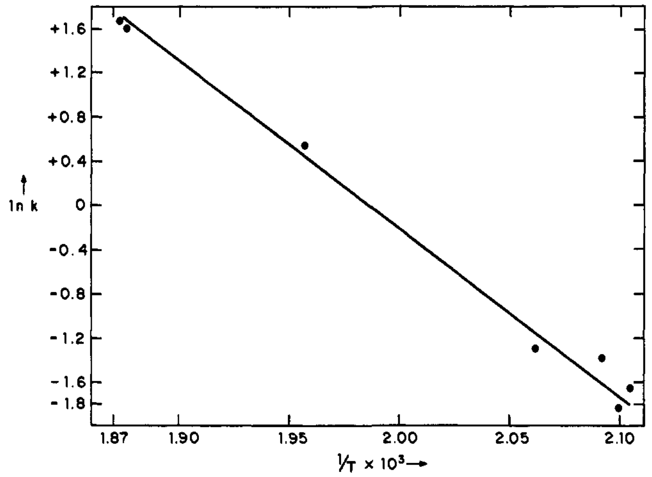

Figure 1. Effect of temperature on the rate of pyrolysis of π-$C_5H_5Rh(C_2H_4)_2$.

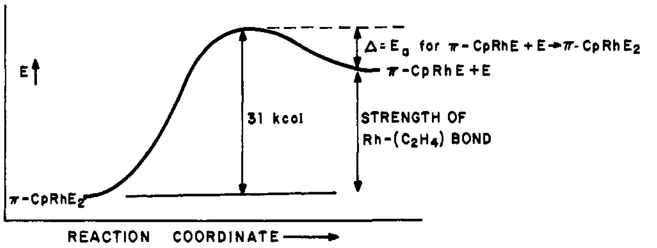

Figure 2. Reaction coordinate for pyrolysis of π-$C_5H_5Rh(C_2H_4)$.

Specifically, with ethylene carrier (10 mm pressure) about 90% of the π-$C_5H_5Rh(C_2H_4)_2$ was recovered whereas under similar conditions with CO_2 carrier (expt no. 1 and 2) only 5% survived. An explanation for these results is that at an ethylene pressure of 10 mm, reaction 10 is slower than the reverse of reaction 9.

$$\pi\text{-}C_5H_5Rh(C_2H_4)_2 \underset{k}{\overset{k}{\rightleftharpoons}} \pi\text{-}C_5H_5Rh(C_2H_4) + C_2H_4 \qquad (9)$$

$$\pi\text{-}C_5H_5Rh(C_2H_4) \xrightarrow{k} C_2H_4 + Rh + ? \qquad (10)$$

Consequently, ethylene can dissociate reversibly from π-$C_5H_5Rh(C_2H_4)_2$.[11] We assume that in pyrolyses with CO_2 carrier, the partial pressure of ethylene is so low (<0.05 mm) that recombination of π-$C_5H_5Rh(C_2H_4)$ and C_2H_4 may be disregarded.

A plot of ln k against $1/T$ (Figure 1) using the data of Table II gives a k-T relationship of $k = 2.8 \times 10^{13} \cdot e^{-31{,}000/RT}$. The activation energy in the exponential term ($E_a = 31$ kcal) is attributed to eq 9, the cleavage of the Rh–C_2H_4 bond in π-$C_5H_5Rh(C_2H_4)_2$. Accordingly, it sets a maximum value of 31 kcal for the strength of the bond by which ethylene is coordinated to rhodium in π-$C_5H_5Rh(C_2H_4)_2$. The relationship between activation energy and bond strength is shown diagrammatically in Figure 2. One needs to know the activation energy for recombination of π-$C_5H_5Rh(C_2H_4)$ and C_2H_4 to complete the calculation.

Determination of dissociation energies by kinetic measurements depends on the assumption that the reverse of eq 11 has zero activation energy. This assumption

$$R_1R_2 \longrightarrow R_1 + R_2 \qquad (11)$$

tion has considerable experimental justification[12] where R_1 and R_2 are atoms or free radicals, but in the present case one of the fragments (ethylene) is a relatively inert species. It has been stated[13] that "the experimental activation energy defined by the expression RT^2 d ln $k/\mathrm{d}T$ gives a fair approximation of the bond dissociation energy, particularly if the experimental frequency factor is close to 10^{13} sec^{-1}." On this criterion we take the strength of the Rh–C_2H_4 coordination bond in π-$C_5H_5Rh(C_2H_4)_2$ to be about 31 kcal.

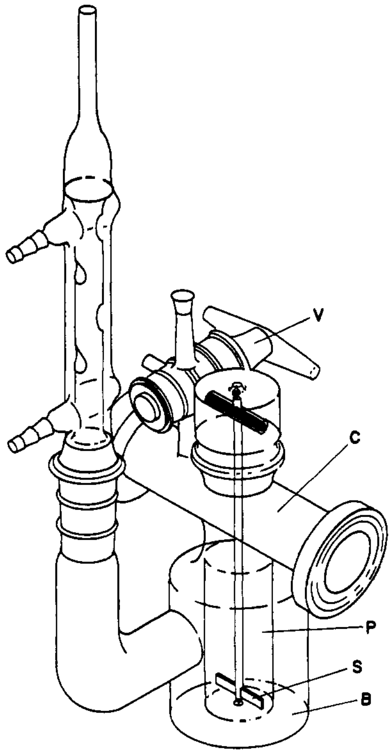

Figure 3. Apparatus for dissociative displacements on π-$C_5H_5Rh(C_2H_4)_2$.

Experimental Section

π-$C_5H_5Rh(C_2H_4)_2$ was prepared from cyclopentadienylsodium and $(C_2H_4)_4Rh_2Cl_2$ according to the method of King.[14]

Displacement of C_2H_4 from π-$C_5H_5Rh(C_2H_4)_2$ by Nucleophiles. The kinetics of this reaction was studied by infrared spectrophotometry using the apparatus shown in Figure 3. This apparatus consists of a gas cell, C (10-cm path length), with NaCl windows sealed in place by Neoprene O-rings and atmospheric pressure. The gas cell had an integral reactor pot, P, with stirrer, S, and was heated by a bath, B, of refluxing liquid, acetic acid for reactions at 118.2°, bis(2-hydroxyethyl) ether for reactions at 136.2°. The gas cell also carried a stopcock, V, fitted with a rubber septum. This served for evacuation of the cell and for the introduction of reactants. The entire apparatus together with an electrically heated oil bath (to maintain the thermostat liquid at reflux) was mounted with C in the beam of a Perkin-Elmer Model 21 infrared spectrometer.

In operation the pot of the cold cell was charged with a solution of the nucleophile in 5.00 ml of solvent (usually diphenyl ether). The windows of the cell were fixed in place and the cell was evac-

---

[11] A specific chemical effect of CO_2 is not involved because the extent of decomposition with ethane as carrier (expt 5, Table II) is about the same as the CO_2 carrier (expt 4, Table II).

[12] T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworths, London, 1958.

[13] M. Szwarc, *Chem. Rev.*, 47, 115 (1950).

[14] R. B. King, *Inorg. Chem.*, 2, 528 (1963).

uated then pressured to 100 mm with N_2.[15] Thermostating liquid was added to the annular reactor jacket and the reactor was positioned in the heating bath and spectrometer beam. When the solution in the reactor had reached reaction temperature, a solution of π-$C_5H_5Rh(C_2H_4)_2$ in 1.0 ml of solvent was added by hypodermic syringe through V into the hot solution of nucleophile in the reactor and the gas cell was scanned continuously at 10.54 μ. (In this cell under these conditions, 1.00 ml of C_2H_4 gas consistently gives an absorptivity increment of 0.23.) Data for calculations were taken from the spectrometer record. The reaction solutions were invariably homogeneous but the final appearance depended on the nucleophile employed. With diethyl fumarate or 1,5-COD bright-yellow reaction solutions resulted but all other ligands gave dark-brown products.

Gas-Phase Pyrolysis of π-$C_5H_5Rh(C_2H_4)_2$. The apparatus used to determine the rate of thermolysis of gaseous π-$C_5H_5Rh(C_2H_4)_2$ is shown in Figure 4. It consisted of a capillary to control CO_2 flow (C), a flask in which π-$C_5H_5Rh(C_2H_4)_2$ was volatilized (F), a pyrolysis tube (T), a manometer to monitor the pressure and flow rate (M), and a trap to collect products (R) which carried a valve to control gas flow (S_1).

The experimental procedure was as follows. A sample of π-$C_5H_5Rh(C_2H_4)_2$ was weighed into the flask F which was then attached to the pyrolysis tube. This tube was wrapped with several layers of lead foil (to promote uniform heating) and heated by a flexible electric tape spaced so that the temperature along the tube was uniform to ±2°. Temperature was measured at the center and 1 in. from both ends of the tube by thermocouples inserted in dimples that extended to the axis of the tube. Carrier gas (usually CO_2) was supplied at a controlled rate. Gross control was provided by the capillary C and fine control by a needle valve (Teflon fluorocarbon resin in glass) at S_1. The rate was monitored by a flowmeter at the supply and by the manometer M. This manometer also measured the pressure in the reactor which was uniform (within 0.5 mm) from the orifice of C to S_1. The apparatus was freed of air and filled with the carrier gas by manipulation of stopcocks S_2 and S_3. S_3 was closed, S_2 opened, and the receiver, R, chilled with liquid nitrogen. S_1 was adjusted to provide the desired pressure for the pyrolysis which produced a flow rate from C of 20–25 ml min^{-1} (25°/1 atm).

Next a heated, thermostated, stirred oil bath was raised to surround F. The carrier gas entered F through a slightly constricted tube which was bent to aim the gas stream at the surface of the sample of π-$C_5H_5Rh(C_2H_4)_2$. The sample was contained in a cylindrical section of F so that a constant surface area was exposed throughout the experiment, thus aiding uniform evaporation. Time was started when the sample of π-$C_5H_5Rh(C_2H_4)_2$ melted (72–73°); 2–4 min more was required to reach the temperature of the heating bath (80–95°).

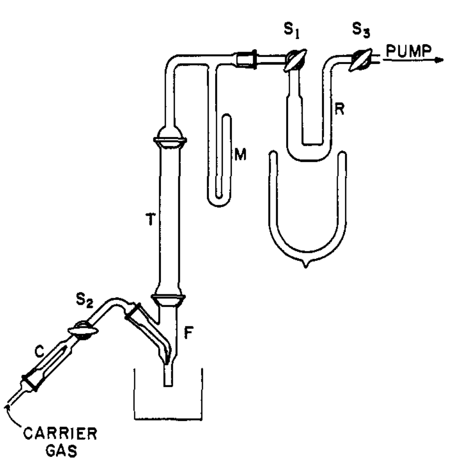

Figure 4. Apparatus for pyrolysis of π-$C_5H_5Rh(C_2H_4)_2$.

Once S_1 had been set, further adjustment was usually unnecessary. Unreacted π-$C_5H_5Rh(C_2H_4)_2$, ethylene produced in the pyrolysis, and carrier gas all condensed in R. Occasionally the connection between T and R was warmed (hot air stream) to ensure that unreacted π-$C_5H_5Rh(C_2H_4)_2$ was swept into R. Pyrolyses required about 1 hr and were stopped before all the π-$C_5H_5Rh(C_2H_4)_2$ in F had evaporated.

Analyses were carried out as follows. R was detached and allowed to warm to room temperature so that the gases it contained could be bled off through concentrated aqueous NaOH. This absorbed CO_2. The residual gas was diluted with air (which was introduced to ensure complete recovery of ethylene) and analyzed by infrared spectrometry.

Unreacted π-$C_5H_5Rh(C_2H_4)_2$ in R and residual π-$C_5H_5Rh(C_2H_4)_2$ in F were measured by nmr. The contents of R and F were recovered with $CDCl_3$ which contained a few per cent $CHCl_3$ to serve as reference signal. The nmr absorptions (π-C_5H_5 protons) of the washings were compared with standard samples of π-$C_5H_5Rh(C_2H_4)_2$ in $CDCl_3$–$CHCl_3$. This provided both a qualitative and quantitative analysis of condensed products. The only nmr absorptions of the product in R were those expected for π-$C_5H_5Rh(C_2H_4)_2$. Between 90 and 95% of the π-$C_5H_5Rh(C_2H_4)_2$ charged could be accounted for either as recovered π-$C_5H_5Rh(C_2H_4)_2$ or ethylene.

Rates of ethylene evolution were calculated with eq 8. The following values were used for C_0 and C. C_0 (initial concentration of reactant) = moles of π-$C_5H_5Rh(C_2H_4)_2$ in R + $^1/_2$(moles of C_2H_4 in R). C (final concentration of reactant) = moles of π-$C_5H_5Rh(C_2H_4)_2$ in R.

---

[15] W. J. Potts, "Chemical Infrared Spectroscopy," Vol. I, Wiley, New York, N. Y., 1963, p 126.