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NUCLEOPHILIC DISPLACEMENT OF ETHYLENE FROM π-$C_5H_5Rh(C_2H_4)_2$

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Summary

It is known that ethylene in π-$C_5H_5Rh(C_2H_4)_2$ is displaced by nucleophiles through a reaction initiated by dissociation of ethylene. A group of nucleophiles (phosphines and phosphites) has now been found which displace ethylene faster than reaction by the dissociative mechanism and at a rate which depends on the concentration of the nucleophile. It is proposed that this reaction involves nucleophilic attack by the incoming ligand and that the cyclopentadienyl ligand assists ethylene displacement by accepting electron density in the transition state.

Introduction

Ethylene is displaced from $acacRh(C_2H_4)_2$ at ambient or lower temperatures by such nucleophiles as PPh_3, CN^- and CO [1], but these compounds do not readily displace ethylene from π-$C_5H_5Rh(C_2H_4)_2$ [2]. On the other hand, electrophiles easily displace ethylene from both $acacRh(C_2H_4)_2$ and π-$C_5H_5Rh(C_2H_4)_2$ [3]. This behavior of Rh^I ethylene complexes is explicable on the basis of electronic structure. Rhodium in $acacRh(C_2H_4)_2$ has the electronic configuration $[Kr]5s^24d^{10}5p^4$ which is two electrons short of rare gas configuration. With only a small increase in energy Rh^I can accept two electrons from a nucleophile to form the transition state of the familiar S_N2 displacement mechanism [4]. However, rhodium in π-$C_5H_5Rh(C_2H_4)_2$ has attained rare gas configuration, $[Kr]$-$5s^24d^{10}5p^6$ (if we assume the cyclopentadienyl ligand contributes six electrons). Consequently an S_N2 displacement of ethylene would be inhibited because promotion of electrons to a much higher energy empty orbital is necessary to

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form the transition state. Displacement of ethylene by electrophiles occurs readily because Rh^I in both $acacRh(C_2H_4)_2$ and π-$C_5H_5Rh(C_2H_4)_2$ has a pair of unshared electrons to donate to a Lewis acid. The formation of this new bond assists the rupture of a $Rh—(C_2H_4)$ bond [3].

A mechanism by which nucleophiles can displace ethylene from π-$C_5H_5Rh(C_2H_4)_2$ involves dissociation of ethylene (eqn. 1 and 2) [2]. This mechanism is encountered above 115°, the temperature necessary for a moderate

$$\pi\text{-}C_5H_5Rh(C_2H_4)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(I)}{\pi\text{-}C_5H_5Rh(C_2H_4)} + C_2H_4 \qquad (1)$$

$$\pi\text{-}C_5H_5Rh(C_2H_4) + L \xrightarrow{k_2} \pi\text{-}C_5H_5Rh(C_2H_4)L \qquad (2)$$

rate of ethylene dissociation (eqn. 1). The 16-electron intermediate readily accepts a nucleophile to form π-$C_5H_5Rh(C_2H_4)L$. The rate of displacement by this mechanism is independent of nucleophile concentration.

In this paper we report the discovery that some phosphites and phosphines displace ethylene from π-$C_5H_5Rh(C_2H_4)_2$ faster than the dissociation (eqn. 1), the rate of reaction is dependent on the nucleophile concentration. Evidence is presented to support a possible explanation.

Results and discussion

Displacement of ethylene from π-$C_5H_5Rh(C_2H_4)_2$

Displacement of ethylene from π-$C_5H_5Rh(C_2H_4)_2$ is conveniently demonstrated by a changing NMR spectrum. The spectrum of π-$C_5H_5Rh(C_2H_4)_2$ in C_6D_6 shows a sharp doublet at 4.90 ppm (from TMS) for π-C_5H_5 protons [J(Rh—H) 0.7 Hz]. Protons of coordinated C_2H_4 give complex doublets centered at 2.74 and 1.22 ppm. Following reaction with a phosphorus-containing ligand new absorptions appear which are associated with C_5H_5 in the new complex (split by P as well as by Rh), free ethylene, coordinated ethylene in the new complex (if only one ethylene is displaced), and coordinated ligand (in most cases shifted in position from the free ligand). The color of the solution changes from yellow to orange.

Results of some displacement experiments are summarized in Table 1. Benzene-d_6 was used as solvent in sealed NMR tubes at 25°C for 4 h. If no displacement was observed the solutions were heated for 1 h at 100° or 130°C. For comparison, the rate of dissociation of ethylene from π-$C_5H_5Rh(C_2H_4)_2$ was evaluated by measuring the rate of its reaction with PPh_3 which yields π-$C_5H_5Rh(C_2H_4)(PPh_3)$ via the dissociation mechanism [2]. At 100°C the rate corresponds to a value of 0.17×10^{-4} sec^{-1} for k_1 or an expected half life for displacement by dissociation of about 16 h. But displacements by most of the nucleophiles listed in Table 1 are more than half complete in 1 h at 100° and with a few, significant displacement was observed at 25°C.

Another group of nucleophiles was found to displace ethylene at 130°C at a rate consistent with the dissociation mechanism. This group includes $AsEt_3$, $SbPh_3$, $AsPh_3$, PPh_3, and $P(C_6F_5)_3$. Finally, $P(t\text{-}Bu)_3$ reacted so slowly with π-$C_5H_5Rh(C_2H_4)_2$ that after 2 h at 135°C only about 30% of the ethylene in

TABLE 1

REACTION OF PHOSPHINES AND PHOSPHITES WITH π-$C_5H_5Rh(C_2H_4)_2$ (0.20 mmol) IN BENZENE-d_6

L	Concentration of L (mmol)	Temp. [a] (°C)	Product composition (%) [c]		
			$CpRhE_2$	CpRhEL	$CpRhL_2$
PF_3 [b]	0.40	<25	0	0	100
PMe_3	0.70	25	80	0	20
		100	0	0	100
$P(OMe)_3$	0.62	25	100	0	0
		100	37	17	45
PEt_3	1.3	25	100	0	0
		100	60	40	0
		130	0	46	64
$P(OEt)_3$	1.4	25	100	0	0
		100	87	13	Trace
		130	0	0	100
$P(OPh)_3$	0.40	25	<100	0	Trace
		100	0	0	100
$P(O\text{-}o\text{-}tolyl)_3$	0.55	25	89	0	11
		100	30	0	70
		130	7	0	93
$P(OCH_2)_3CC_2H_5$	0.69	25	98	0	2
		100	19	0	81
		130	0	0	100
$P(n\text{-}Bu)_3$	0.45	25	100	0	0
		100	81	19	0
		130	14	87	0

[a] Reaction times were 1 h at 100 and 130°C and 4 h or more at 25°C [b] A preliminary communication describing ethylene displacement from π-$C_5H_5Rh(C_2H_4)_2$ by PF_3 appeared while this work was in progress [14]. [c] Calculated from integrated areas of the NMR spectra.

π-$C_5H_5Rh(C_2H_4)_2$ had been displaced. Possibly because of steric effects, displacement of C_2H_4 by $P(t\text{-}Bu)_3$ is kinetically or thermodynamically disfavored.

It is apparent that for two reasons displacements of ethylene from π-$C_5H_5Rh(C_2H_4)_2$ by the nucleophiles of Table 1 cannot be accommodated by the dissociation mechanism. First, there are substantial differences in rates for different displacing ligands, which would not be expected if ethylene dissociation were rate determining. Secondly the rate of displacement by these ligands is significantly faster than the rate of ethylene dissociation from π-$C_5H_5Rh(C_2H_4)_2$. In order to characterize the appropriate mechanism, we examined the effect of ligand concentration on the rate of displacement by measuring the rate of disappearance of π-$C_5H_5Rh(C_2H_4)_2$ (by NMR) and the rate of liberation of ethylene (by IR and NMR). We found that with the compounds listed in Table 1 the rate of displacement increased when the concentration of displacing ligand increased but the relation is generally complex.

Two sources of complication were anticipated: *(1)*. Dual mechanisms - in reactions above 100°C dissociative and S_N2 mechanisms may compete. *(2)*. Dual reactions when the rate of liberation of ethylene is measured, since ethylene is generated by two reactions (eqn. 3 and 4) whose relative rates differ with L (Table 1).

$$\pi\text{-}C_5H_5Rh(C_2H_4)_2 + L \rightarrow \pi\text{-}C_5H_5Rh(C_2H_4)L + C_2H_4 \tag{3}$$

$$\pi\text{-}C_5H_5Rh(C_2H_4)L + L \rightarrow \pi\text{-}C_5H_5RhL_2 + C_2H_4 \tag{4}$$

The least complicated kinetics are expected in reactions which occur at temperatures substantially below 100°C and when the rate of disappearance of π-$C_5H_5Rh(C_2H_4)_2$ is monitored. Analysis by NMR of a solution of π-$C_5H_5Rh(C_2H_4)_2$ (0.20 mmol) and P(O-*o*-tolyl)$_3$ (0.52 mmol) in 0.4 ml C_6D_6 shows that at 79°C, π-$C_5H_5Rh(C_2H_4)_2$ disappears at an initial rate of 0.86×10^{-4} mmol sec^{-1}. When the amount of P(O-*o*-tolyl)$_3$ was nearly doubled (1.03 mmol), the rate was slightly over twice as fast (1.8×10^{-4} mmol sec^{-1}). This corresponds to first order dependence on phosphite concentration.

Displacement by the slower reacting $P(OC_2H_5)_3$, (see Table 1) is more complex. π-$C_5H_5Rh(C_2H_4)_2$ disappears about 40% faster when the concentration of $P(OC_2H_5)_3$ is doubled (Table 2, Exp. 2 and 4 vs. 3 and 5). Since this reaction was studied at 100°C, it is expected that the dissociative mechanism will be involved to some degree and a correction should be made for it (column 5, Table 2). The corrected rate constants are still not linearly dependent on $P(OC_2H_5)_3$ concentration. It appears that the rates are not affected by the ethylene which accumulates by displacement since introduction of uncoordinated ethylene does not affect the rates (Table 2, Exp. 4 and 5 vs. 2 and 3).

The dependence of the rate of displacements by $P(OCH_2)_3CC_2H_5$ and $P(OCH_3)_3$ on phosphite concentration at 100°C was similar to that found with $P(OC_2H_5)_3$.

Character of bonding in the transition state

The kinetics suggest an activated complex which is an adduct of π-$C_5H_5Rh(C_2H_4)_2$ and the displacing phosphite or phosphine. As was mentioned in the introduction, this requires promotion of the unshared pair of *sp*^{3} electrons of the entering phosphorus compound into a higher energy orbital. One possibility would involve establishing a σ—π bond between Rh and P. Since aliphatic amines do not have *d* orbitals available for σ—π bonding an attempt was made to test the hypothesis by trying to displace ethylene from π-$C_5H_5Rh(C_2H_4)_2$ with amines such as NH_3, NMe_3, NEt_3, $(PhCH_2)_3N$, and pyridine. Displacement of ethylene did not occur at 100°C but the experiments do not provide a valid

TABLE 2

RATE OF REACTION OF π-$C_5H_5Rh(C_2H_4)_2$ with $P(OC_2H_5)_3$ [a]

Exp.	π-C_5H_5Rh-$(C_2H_4)_2$ (mmol)	$P(OC_2H_5)_3$ (mmol)	$k \times 10^4$ (sec^{-1})	$(k_1 - 0.17^b) \times 10^4$ (sec^{-1})
1	0.20	None	0.20; 0.16, 0.15	
2	0.20	0.50	1.9	1.7
3	0.20	1.02	2.5	2.3
4 [c]	0.21	0.50	1.8	1.6
5 [c]	0.20	1.04	2.6	2.4

[a] At 100°C. Rate of disappearance of π-$C_5H_5Rh(C_2H_4)_2$ by NMR spectroscopy. [b] Average value for the rate constant for reaction of π-$C_5H_5Rh(C_2H_4)_2$ with PPh_3. [c] Contain 0.41 mmol of C_2H_4.

test of the hypothesis. It appears that complexes of the type π-$C_5H_5Rh(C_2H_4)(NR_3)$ or π-$C_5H_5Rh(NR_3)_2$ may be thermodynamically unstable since they were not formed (through the dissociative mechanism) from π-$C_5H_5Rh(C_2H_4)_2$ and amines at 130°C. Possibly the π-C_5H_5Rh group is so electron-rich that it can form strong bonds only with bases that can accept electrons through formation of a π-bond.

An alternative test for the hypothesis of electron promotion to a π-bond of the incoming ligand was made by studying the reaction of π-$C_5H_5Rh(C_2H_4)_2$ with olefinic compounds, known to be π-bonders. It was found that vinyl acetate, methyl acrylate, acrylonitrile, propylene, maleic acid and dimethyl fumarate all displace one or two ethylene ligands from π-$C_5H_5Rh(C_2H_4)_2$ but at a rate which is appropriate for the dissociative mechanism. Evidence has been reported [6] that π-bonding does *not* assist the displacement of ethylene from $acacRh(C_2H_4)_2$ by C_2F_4.

We prefer an explanation first proposed by Schuster-Woldan and Basolo [7] to account for the related nucleophilic displacement of CO from π-$C_5H_5Rh(CO)_2$. They suggested the electrons of the incoming nucleophile were accommodated by conversion of π-C_5H_5 to a $C_5H_5^-$ ligand. One possibility would involve reorganization of the *pentahapto*-π-cyclopentadienyl ligand to a *trihapto* allylic ligand[*]. If it is assumed that the cyclopentadienyl ligand is involved, nucleophilic displacement should be facilitated by electronegative substituents. A comparison was made of π-$C_5H_5Rh(C_2H_4)_2$ with π-$C_5H_4CNRh(C_2H_4)_2$, π-$C_5H_4COOCH_3Rh(C_2H_4)_2$, and π-$C_5(CH_3)_5Rh(C_2H_4)_2$ by finding the temperature at which ethylene was displaced by various phosphorus containing ligands (Table 3). Ethylene is displaced more readily from π-$C_5H_4CNRh(C_2H_4)_2$ than from π-$C_5H_5Rh(C_2H_4)_2$. On the other hand, it is more difficult to displace ethylene from π-$C_5(CH_3)_5Rh(C_2H_4)_2$. The $—CO_2CH_3$ substituent appears to have little effect on the rate of ethylene displacement. This is consistent with Schuster-Woldan and Basolo's hypothesis; the only apparent discrepancy involves PF_3 which displaces ethylene

TABLE 3

EFFECT OF π-CYCLOPENTADIENYL LIGAND SUBSTITUENTS UPON THE EASE[a] OF ETHYLENE DISPLACEMENT

L	π-C_5H_5	π-C_5H_4CN	π-$C_5H_4CO_2CH_3$	π-$C_5(CH_3)_5$
PPh_3	130/0.25	25/2.5		130/ca. 0.1[b]
$P(n\text{-}Bu)_3$	100/1.5	25/2.0	100/0.5	130/0.15
$P(OEt)_3$	100/2	25/0.25		130/0.25
PMe_3	25/5	25/<0.05	25/<1	130/0.25
PF_3	25/<0.05	25/0.5		25/<0.05

[a] Temperature/time (h) required for reaction of about 25% of 1 mmol π-(X-Cp)$Rh(C_2H_4)_2$ mixed with 2 to 3 mmol of ligand. [b] Barely perceptible reaction after 1 h at 100°C.

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[*] A referee cited a description [8] of the concept of a (*trihapto*-cyclopentadienyl)—metal bond as "mythical". This opinion is based on the assumption that the ring in a $(h^3\text{-}C_5H_5)M$ group would be a regular plane pentagon. Since no experimental or theoretical evidence was presented to support the assumption of regular planarity we continue to regard the $(h^3\text{-}C_5H_5)M$ group as a possible configuration.

faster from π-$C_5H_5Rh(C_2H_4)_2$ than from π-$C_5H_4CNRh(C_2H_4)_2$. Possibly as a consequence of its high electronegativity [9], PF_3 is electrophilic and electron promotion follows a path that is different from that taken by other phosphites and phosphines.

The kinetics of displacements from π-$C_5H_4CNRh(C_2H_4)_2$ were studied to learn whether the mechanism was bimolecular or dissociative. (Conceivably a substantially weaker Rh—C_2H_4 bond could lead to dissociative displacement at a low temperature.) Reaction was followed by measuring the amount of ethylene displaced through its infrared absorbance [2].

It was found (Table 4) that with all the phosphorus-containing ligands the rate increased as the concentration of ligand was increased. In displacements with PPh_3 the rate is nearly proportional to the concentration of PPh_3 (note the figures in column 4 for exp. 1, 2, 3 and 4 are almost constant.) This dependence on ligand concentration (corresponding to a S_N2 mechanism) is a striking change from the reaction with π-$C_5H_5Rh(C_2H_4)_2$ whose rate is independent of phosphine concentration (hence, dissociative mechanism). The rates of reaction of π-$C_5H_4CNRh(C_2H_4)_2$ with other phosphorus-containing ligands increase with, but are not proportional to, ligand concentration.

Displacement of ethylene from π-$C_5H_4CNRh(C_2H_4)_2$ by dimethyl fumarate or tolunitrile is believed to involve a dissociative mechansim since the rates are about the same as the rate of release of ethylene by thermolysis (exp. 16, 17 and 18, Table 4).

Attempts to detect an adduct complex of π-$C_5H_5RhL_2$ and L'

The accepted [4] mechanism for S_N2 displacement of ligands from square

TABLE 4

ETHYLENE DISPLACEMENT FROM π-$C_5H_4CNRh(C_2H_4)_2$ [a]

Exp.	Nucleophile (mmol)	$k \times 10^3$ (sec^{-1})	$\frac{k_1 - 0\ 08}{\{\text{mmol of L}\}} \times 10^3$
1	PPh_3 (0.20)	0.48; 0.46	0.20; 0.19
2	PPh_3 (1.00)	1.70; 1.68	0.16; 0.16
3	PPh_3 (2.00)	2.83, 2.77	0.14, 0.13
4	PPh_3 (2.20)	3.38	0.15
5	$P(n\text{-}Bu)_3$ (0.24)	2 30; 2.10	9 3; 8.4
6	$P(n\text{-}Bu)_3$ (0.92)	4.40	4.7
7	$P(n\text{-}Bu)_3$ (1.04)	5.08	4.8
8	$P(n\text{-}Bu)_3$ (2.00)	10.25	5.1
9[b]	$P(OCH_2)_3CC_2H_5$ (0.22)	3.13; 3.55	14.2; 16.1[b]
10[b]	$P(OCH_2)_3CC_2H_5$ (0.54)	6.03	11.2[b]
11[b]	$P(OCH_2)_3CC_2H_5$ (0.83)	6 78	8.2[b]
12	$Ph_2PCH_2CH_2PPh_2$ (0.20)	2.40, 2.33	1.2; 1.1
13	$Ph_2PCH_2CH_2PPh_2$ (1.00)	5.03	5.0
14	$P(O\text{-}o\text{-}tolyl)_3$ (0.16)	0.22	0.88
15	$P(O\text{-}o\text{-}tolyl)_3$ (2.00)	0.92	0.42
16	Dimethyl fumarate (1.00)	0.07	
17	p-$CH_3C_6H_4CN$ (2.0)	0.08	
18	None	0.08	

[a] In diphenyl ether at 100°C using 0.10 mmole of π-$C_5H_4CNRh(C_2H_4)_2$. [b] Reaction run at 56.2°C. Quotients in column 4 are k_1/mmol of ligand with no correction for dissociative reaction.

planar complexes has received important confirmation through the identification of related 5-coordinate compounds [10]. We have attempted unsuccessfully to find evidence of an adduct intermediate in nucleophilic displacements on π-$C_5H_5RhL_2$. The electronic spectra of methanol solutions of π-$C_5H_5Rh(C_2H_4)_2$ and $P(OCH_2)_3CC_2H_5$ do not provide evidence of a third species at 25°C prior to displacement.

The ^1H and ^{31}P NMR spectra of solutions of π-$C_5H_5Rh(C_2H_4)_2$ and PF_3 in CD_2Cl_2 were examined between −120° and 0°C. (Ethylene displacement is observable at −40°C). No evidence was found of an intermediate. The ^1H and ^{31}P NMR spectra of solutions of PF_3 with π-C_5H_5Rh(1,5-COD), π-C_5H_5Rh(1,5-hexadiene) or π-C_5H_5Rh(norbornadiene) were also examined between −80° and 0°C in the expectation that a chelate diene ligand might stabilize the adduct. An adduct was not detected. Displacement of 1,5-cyclooctadiene was observed at −20°, 1,5-hexadiene at −80° and norbornadiene at −30°C.

Displacements from miscellaneous π-$C_5H_5Rh(Olefin)(Olefin')$ complexes

Olefin displacements from π-$C_5H_5Rh(C_2H_4)(CH_2{=}CHOCOCH_3)$, π-$C_5H_5Rh(CH_2{=}CHCN)_2$, or π-$C_5H_5Rh(C_2H_4)(CH_2{=}CHF)$ by PMe_3 or PPh_3 follow the same mechanism patterns as π-$C_5H_5Rh(C_2H_4)_2$. Trimethyl phosphine reacts in one hour at 100°C with both π-$C_5H_5Rh(C_2H_4)(CH_2{=}CHF)$ [to give π-$C_5H_5Rh(PMe_3)_2$] and π-$C_5H_5Rh(CH_2{=}CHCN)_2$ [to give π-$C_5H_5Rh(CH_2{=}CHCN)(PMe_3)$ and π-$C_5H_5Rh(PMe_3)_2$]. Although dependence on PMe_3 concentration was not determined, the relatively mild conditions suggest an S_N2 mechanism.

Triphenyl phosphine also displaces one acrylonitrile ligand from π-$C_5H_5Rh(CH_2{=}CHCN)_2$ at 100°C (S_N2 displacement ?) but requires a higher temperature (135°C) to displace vinyl fluoride from π-$C_5H_5Rh(C_2H_4)(CH_2{=}CHF)$ or convert π-$C_5H_5Rh(C_2H_4)(CH_2{=}CHOCOCH_3)$ to π-$C_5H_5Rh(PPh_3)_2$. It is inferred that ethylene is displaced first from π-$C_5H_5Rh(C_2H_4)(CH_2{=}CHOCOCH_3)$ since π-$C_5H_5Rh(C_2H_4)(PPh_3)$ does not react with PPh_3 and could not yield π-$C_5H_5Rh(PPh_3)_2$. Accordingly competitive displacements in these two compounds correspond to the following decreasing ease of displacement: vinyl fluoride > ethylene > vinyl acetate.

Conclusions

We conclude that four mechanisms are available for displacement of ethylene from its complexes with Rh^I. Two are fast with half-lives of the order of seconds or minutes at −80°C. These are electrophilic or nucleophilic displacements on square planar complexes or electrophilic displacements from π-$C_5H_5Rh(C_2H_4)_2$. The other two are slow with halflives of the order of hours at 25° to 125°C. These have been observed only with compounds π-$C_5H_5Rh(olefin)_2$ and involve either initial dissociation of olefin or a nucleophilic mechanism which requires promotion of electrons to higher energy orbitals. It appears most likely that the higher energy orbital involved in the nucleophilic displacement is associated with the cyclopentadienyl ligand.

Experimental

Materials

π-$C_5H_5Rh(C_2H_4)_2$ was prepared from cyclopentadienyl sodium and $(C_2H_4)_4Rh_2Cl_2$ [11]. π-C_5H_5Rh(1,5-COD) and π-C_5H_5Rh(norbornadiene) were obtained by displacement of ethylene from π-$C_5H_5Rh(C_2H_4)_2$. π-C_5H_5Rh(1,5-hexadiene) was prepared by R.A. Schunn [1]. π-$C_5H_4CNRh(C_2H_4)_2$ and π-$C_5H_4CO_2CH_3Rh(C_2H_4)_2$ were made from the substituted cyclopentadienyl thallium compounds and $(C_2H_4)_4Rh_2Cl_2$ [12]. π-$C_5(CH_3)_5Rh(C_2H_4)_2$ was synthesized by Maitlis's method [13].

Kinetics of ethylene displacement

These were studied using infrared and NMR spectroscopy. The infrared technique has been described [2]. The apparatus was modified by placing a short water cooled condenser between the reactor pot and the gas cell to prevent solvent condensation on the cell windows. Thermostat liquids were water at 100° and acetone at 56.2°C.

In the NMR experiments, tubes were charged, chilled, evacuated and sealed, then heated in a steam bath and the spectra recorded periodically. The amount of π-$C_5H_5Rh(C_2H_4)_2$ which had reacted was found through comparison of the integrated areas of π-C_5H_5 protons in reactant and product(s).

Generally, the sets of data (time vs. extent of reaction) were analyzed using a polynomial regression computer program (of maximum degree 9) to obtain an equation for the rate of reaction. The derivative of this equation at time zero was used to calculate the rate constant. The goodness-of-fit is indicated by the observation that in all experiments the equation, a second degree polynomial, gave a Calcomp plotted curve whose normal deviation from experimental points was less than 3% of the final value for extent of reaction. In a few experiments the sets of data were plotted and the slope of the tangent to the curve at t = zero was used to calculate rate constants.

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