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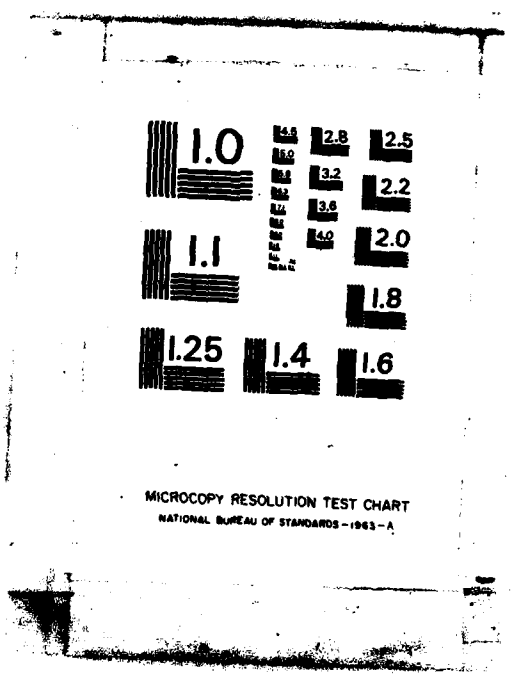
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H/D Exchange in the Reaction of D_2 with Bis(triphenylphosphite) (acetylacetonato)rhodium(I), $Rh(P(OPh)_3)_2(acac)$

by

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$P(OPh)_3$ being the same as that into acac at all stages of the H/D exchange process. At 60°C, deuterium incorporation into $P(OPh)_3$ is initially more rapid than that seen into the acac ligand. The initial rate of deuterium incorporation into $P(OPh)_3$ by 1 in d_6-benzene under D_2 at 60°C proceeds with a first order rate constant of 9.6×10^{-5} sec $^{-1}$. A mechanism for this exchange process is proposed.

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H/D Exchange in the Reaction of D_2 with Bis(triphenylphosphite)(acetylacetonato)rhodium(I). $Rh(P(OPh)_3)_2(acac)$

Bryan C. Whitmore and Richard Eisenberg*

ABSTRACT

The reaction of $Rh(P(OPh)_3)_2(acac)$ (1) with D_2 in benzene has been studied by ^1H NMR spectroscopy, and complex 1 has been found to undergo H/D exchange at the ortho positions of the coordinated phosphite ligands and at the central methine position of the acetylacetonate ligand. At 79°C, the exchange reaction proceeds with the extent of deuterium incorporation into $P(OPh)_3$ being the same as that into acac at all stages of the H/D exchange process. At 69°C, deuterium incorporation into $P(OPh)_3$ is initially more rapid than that seen into the acac ligand. The initial rate of deuterium incorporation into $P(OPh)_3$ by 1 in d_6-benzene under D_2 at 69°C proceeds with a first order rate constant of 9.6×10^{-6} sec^{-1}. A mechanism for this exchange process is proposed.

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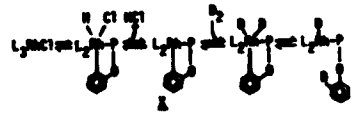
Introduction

Rhodium(I) complexes containing a single acetylacetonate (acac) ligand of the type RhLL'(acac), where L,L'=CO,PPh_3,C_2H_4, were first reported in 1964.[1] Since that time numerous complexes containing different ligands, L, have been reported and studied. Many of these complexes are used as catalyst precursors for industrially important reactions such as olefin hydrogenation[2] and hydroformylation[3,4], and have appeared in numerous patents.[5] One acac complex recently reported to catalyze arene hydrogenation is the phosphite complex, $Rh(P(OPh)_3)_2$-(acac), 1.[6] Related rhodium(I) complexes containing phosphite ligands such as $Rh(P(OPh)_3)_3Cl$ and $Rh(P(OPh)_3)_4^+$ have been studied by Bergfield and Parshall,[7] and have been found to undergo H/D exchange under D_2 at the ortho positions of the coordinated triphenyl phosphite ligands.[7] This exchange reaction has been proposed by Parshall to proceed through an ortho-metallated intermediate X as shown in equation (1). Based on the reactivity of known rhodium(I) phosphite



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complexes and the utilization of Rh(I)-acac complexes as homogeneous catalyst precursors, we have examined the reaction of complex 1, $Rh(P(OPh)_3)_2(acac)$, with H_2 and D_2. The results obtained from these reactions may aid in the elucidation of mechanisms for reactions catalyzed by complex 1 and other rhodium(I) acetylacetonate complexes.

Experimental

$Rh(P(OPh)_3)_2(acac)$ was prepared by the literature method.[8] All experiments were performed in sealed NMR tubes in d_6-benzene. ^1H NMR spectra were recorded on a Bruker WH-400 400 MHz instrument with chemical shifts reported in ppm relative to TMS.

General procedure for ^1H NMR experiments. The rhodium complex, $Rh(P(OPh)_3)_2(acac)$, is placed in a 5 mm NMR tube which is evacuated on a high vacuum line. The tube is cooled to -196°C, liquid reactants (acetylacetone, $P(OPh)_3$) and d_6-benzene (0.5mL) are condensed into the NMR tube and the sample is then flame sealed under an H_2 or D_2 atmosphere. The reaction solution is heated at the indicated temperature and monitored by ^1H NMR spectroscopy. Specific reaction conditions are summarized in Table I.

Phosphite exchange reaction. The NMR tube from reaction 1 (Table I) is broken open in air at the completion of the exchange reaction (96% deuterium incorporation). Half of the d_6-benzene solution of complex d_{13}-1 (2.7μmol) is treated with $P(OPh)_3$ (1.5μL, 5.7μmol) and its ^1H NMR spectrum is recorded immediately. The deuterium content of the ortho position of coordinated $P(OPh)_3$ is 46% within 5 minutes of mixing as determined through comparison of its integrated intensity with the integrated areas of the meta and para positions. The resonance due to the central methine position of acac remains unchanged.

Results and Discussion

H/D exchange at 75°C. When a d_6-benzene solution of $Rh(P(OPh)_3)_2(acac)$, 1, is heated at 75°C under D_2(405 torr) (Reaction 1, Table I) a gradual change is observed in the 6.8-7.5 ppm region of its ^1H NMR spectrum as shown in Figure 1. The aromatic region in the initial spectrum, (a), contains three multiplets assignable to the coordinated triphenyl phosphite ligands. The ortho hydrogens appear at 7.48ppm, and are split into a doublet by the meta hydrogens (J_{o-m}=8.0Hz). The meta hydrogens give rise to a doublet of doublets at 7.01 ppm, and the

para hydrogens appear as a triplet at 6.85 ppm (J_{m-p}=7.4Hz). Within several hours of heating the complex under D_2, the meta hydrogen resonance becomes increasingly complicated and the ortho hydrogen resonance decreases in integrated intensity compared to the meta and para hydrogens (spectrum (b)). In spectrum (c) the resonance due to the ortho hydrogens is nearly gone, and the meta hydrogen resonance now appears as a doublet (J=7.4Hz). The para hydrogen resonance remains unchanged throughout this reaction. These spectral changes are consistent with deuterium substitution into the ortho positions of the coordinated triphenyl phosphite ligands, and are similar to spectral changes in previous reports of H/D exchange in related Rh(I) triphenyl phosphite complexes.[7,9] However, as deuterium is incorporated into the phosphite ligand in $Rh(P(OPh)_3)_2(acac)$, there occurs a concomitant decrease in the integrated intensity of the central methine proton of the acetylacetonate ligand indicating deuterium substitution into this position as well. At any point during this D substitution, the percentage of protons remaining in the methine position of the acac ligand is the same as the percentage of hydrogens seen in the ortho positions of the coordinated $P(OPh)_3$ ligand (see Figure 2). The only resonances observed in this exchange reaction are those attributable to $Rh(P(OPh)_3)_2(acac)$ and its partially deuterated homologs. When the reaction is carried out in d_6-benzene under H_2, no evidence of hydride formation is observed, nor is any evidence of free acetylacetone or $P(OPh)_3$ obtained. Since complex 1 is the only species seen in solution by ^1H NMR spectroscopy, any intermediates in the exchange process are present in only very small concentrations. The fact that the rate of D-incorporation into acac and $P(OPh)_3$ is the same indicates that a species common to both exchange processes, or related by ancillary equilibria, exists. If the two exchange processes were completely independent, proceeding without a common intermediate or equilibrium-related species, then two distinct rates of D-incorporation - one for $P(OPh)_3$

and one for acac - would be observed. This is clearly not the case for $Rh(P(OPh)_3)_2(acac)$. In addition, the fact that the extent of deuteration at the methine position of acac is always the same as that at the ortho positions of $P(OPh)_3$ indicates that the rate of D-incorporation into the latter is greater than that into acac. If the reverse were true - ie, if D-incorporation into acac were faster than the deuteration of $P(OPh)_3$ - then the methine proton resonance would decrease in intensity more rapidly than the o-proton resonance of $P(OPh)_3$. This conclusion concerning relative rates of deuterium incorporation is supported by studies of exchange at 60°C described below.

In order to probe more fully the nature of the H/D exchange reactions at 75°C, we performed additional reactions in the presence of added $P(OPh)_3$ and/or acetylacetonate ligand. When complex 1 is placed under D_2 in the presence of 1 equiv $P(OPh)_3$, deuterium incorporation into both coordinated and free $P(OPh)_3$ is observed, as well as into the methine position of the acac ligand. A small amount of free acetylacetone is also detected. Similarly, when 1 is heated at 75°C under D_2 with 2.7 equiv of Hacac added, exchange into both coordinated and free acac is seen, as well as into the ortho positions of coordinated $P(OPh)_3$. H/D exchange into free and coordinated ligands is also seen when the same reaction is run with 1 equiv $P(OPh)_3$ and 4 equiv Hacac added. Clearly, ligand exchange is a factor in analyzing the H/D exchange reactions in the $Rh(P(OPh)_3)_2(acac)$ system.

The facility of phosphite exchange with 1 is demonstrated by the following reaction. When 2.1 equivalents of $P(OPh)_3$ are added to the d_6-benzene solution of d_{13}-1 (90%, formed at the completion of reaction 1, Table I) at room temperature there is an immediate reappearance in the ^1H NMR spectrum of the resonance due to the ortho positions of coordinated $P(OPh)_3$. Within five minutes, the integrated intensity of the ortho protons from coordinated $P(OPh)_3$ indicates a

46% deuterium content which corresponds to complete scrambling of labelled and unlabelled $P(OPh)_3$ ligands (equation 2).

$$(d_2\text{-PhO})_3P \quad (d_2\text{-PhO})_3P$$
$$\diagdown \quad \diagup \qquad \diagdown \quad \diagup$$
$$Rh(acac) + P(OPh)_3 \rightleftharpoons Rh(acac) + P(O\text{-}d_2\text{-}Ph)_3 \qquad (2)$$
$$\diagup \quad \diagdown \qquad \diagup \quad \diagdown$$
$$(PhO)_3P \quad (PhO)_3P$$

The facile exchange of free and coordinated phosphite ligands in this system contrasts with a recent study using ^{31}P NMR spectroscopy which concludes that phosphite exchange for 1 does not occur or occurs only very slowly. While this ligand exchange may be too slow to be observed by room temperature NMR line broadening, it is readily observed at room temperature using labelled phosphite ligands. The results of this $P(OPh)_3$ exchange experiment clearly show that 1 exchanges $P(OPh)_3$ more rapidly than 1 undergoes deuterium incorporation reactions. When the reaction mixture ($1+D_2$) is maintained at room temperature (23°C) there is no change in its ^1H NMR spectrum over the course of several hours. Deuterium incorporation into the coordinated ligands is detected only when the benzene solution of $1 + D_2$ is heated.

<u>H/D exchange at 60°C.</u> When the reaction of $Rh(P(OPh)_3)_2(acac)$ with D_2 is carried out at 60°C, changes are seen in its ^1H NMR spectrum similar to those observed at 75°C. However, at this lower temperature, D-incorporation into the phosphite ligand is initially much more rapid than substitution into the acac ligand as illustrated in Table II. Thus, deuterium substitution occurs primarily on the $P(OPh)_3$ ligand during the early stages of the exchange reaction at 60°C. This reaction, shown as equation 3, can be considered a simple isotope exchange

$$D_2 + \text{H-Rh(P(OPh)}_2\text{(P(OPh)}_3\text{)(acac)} \rightleftharpoons HD + \text{D-Rh(P(OPh)}_2\text{(P(OPh)}_3\text{)(acac)} \qquad (3)$$
$$\text{A} \qquad\qquad \text{B}$$

reaction, which is the first of a series of H/D exchanges of the general form d_x-$\underline{1}$ + D_2 ⇌ d_{x+1}-$\underline{1}$ + HD, where x=0-12. However, as the exchange process continues, the kinetics of H/D exchange grows in complexity due to the increasing probability of back-reactions and degenerate exchanges as shown in eqns (4)-(9). After several exchanges have occurred there

back-reactions

$$(D_x)\text{-}\underline{1} + HD \rightleftharpoons (D_{x-1})\text{-}\underline{1} + D_2 \quad (4)$$

$$(D_x)\text{-}\underline{1} + H_2 \rightleftharpoons (D_{x-1})\text{-}\underline{1} + HD \quad (5)$$

degenerate exchanges

$$(D_xD^*)\text{-}\underline{1} + D_2 \rightleftharpoons (D_xD)\text{-}\underline{1} + DD^* \quad (6)$$

$$(D_xD^*)\text{-}\underline{1} + HD \rightleftharpoons (D_xD)\text{-}\underline{1} + HD^* \quad (7)$$

$$(D_xH^*)\text{-}\underline{1} + HD \rightleftharpoons (D_xH)\text{-}\underline{1} + H^*D \quad (8)$$

$$(D_xH^*)\text{-}\underline{1} + H_2 \rightleftharpoons (D_xH)\text{-}\underline{1} + HH^* \quad (9)$$

is an increase first in the concentration of HD and subsequently in the concentration of H_2. Indeed, during the exchange reactions both HD and H_2 are detected by ^{1}H NMR spectroscopy. A 1:1:1 triplet (J = 42 Hz) at 4.62 ppm is seen for HD, while H_2 gives rise to a singlet at 4.45 ppm (in d_6-benzene). As the concentrations of these molecules increase, there is an increase in the likelihood that they will become involved in the exchange processes (4) - (9). Although D_2 is present in the excess in the gas phase above the reaction solutions, its concentration in the benzene solutions is nearly the same as that of the rhodium complex, $\underline{1}$. For example, in reaction 5 (Table I) under 517 torr pressure the concentration of D_2 in solution is roughly 2mM while the concentration of $\underline{1}$ is 4.0mM. Due to the low surface area of benzene in the NMR tube, as D_2 is consumed in solution, it may

not be immediately replaced by D_2 from the gas phase and the relative concentrations of HD and H_2 become larger than expected. Thus as the reaction proceeds, it becomes mass transfer limited.

Despite the obvious complexity of this exchange process, an estimate of the rate of H/D exchange in coordinated $P(OPh)_3$ during the early stages of the reaction $\underline{1}$ + D_2 can be obtained using eqn (10) derived by Calvin[10] and other workers[11] which deals with the rate of simple isotope exchange.

$$\ln \frac{[A_0]}{[A]} = \frac{a}{a+b}(a+b)t = kt \quad (10)$$

a and b are defined in equation (3)

$[A_0]$ = concentration of A at t=0

$$a = [D_2] + [HD]$$

$$b = [A] + [B]$$

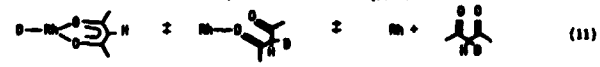
A plot of $\ln([A_0]/[A])$ vs t for reaction 6, shown in Figure 3, is linear during the initial stages of the reaction, and yields a value for k in eqn (10) of 9.6×10^{-6} sec^{-1}.

Mechanism of H/D Exchange.

Any mechanism drawn for the H/D exchange reactions of complex $\underline{1}$ must account for the results obtained in the experiments described above which are summarized as follows: (1) there is a facile room temperature exchange of free and coordinated triphenyl phosphite; (2) deuterium is incorporated into both $P(OPh)_3$ and acetylacetonate ligands; (3) deuterium is incorporated into both free and coordinated ligands; (4) the relative rates of D-substitution into $P(OPh)_3$ and acac are the same at 70°C.; (5) at 60°C, the rate of deuteration of $P(OPh)_3$ is faster than that of acac; (6) during the reaction of $\underline{1}$ with D_2 or H_2, no species except for $\underline{1}$ is detected by ^{1}H NMR spectroscopy; and (7) during the reaction of $\underline{1}$ with D_2 in the presence of excess $P(OPh)_3$, free acetylacetone is observed by ^{1}H NMR.

These facts lead us to the proposed mechanism for H/D exchange which is shown in Scheme I.

The incorporation of deuterium into the ortho-position of coordinated $P(OPh)_3$ must involve the activation of both the D_2 molecule and the ortho-phenyl position of the phosphite ligand. Both of these processes occur most logically via oxidative additions to Rh(I) centers. These oxidative additions have been proposed by Parshall to explain H/D exchange in similar rhodium phosphite complexes.[7] The incorporation of deuterium into coordinated acac on the other hand requires the formation of acetylacetone, either free or weakly coordinated, via the reductive elimination of Dacac from a Rh-D species as shown in equation (11).



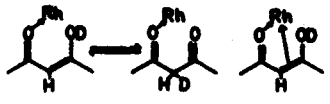
(11)

Following the first oxidative addition, which is either that of D_2 or of the ortho-phenyl C-H bond to the Rh(I) center, a reductive elimination must occur to regenerate a rhodium(I) center and allow the second oxidative addition step to take place. This intermediary reductive elimination is most likely that of Dacac as shown in equation (11). Two sequences of reactions are therefore possible in this system. The first sequence begins with the oxidative addition of D_2 to complex **1**, while the second starts with the orthometallation of the phosphite ligand to the rhodium(I) center.

If the oxidative addition of D_2 to complex **1** were to occur first, then one forms species **6**. The reductive elimination of Dacac from **6** yields species **5** which can then undergo reversible orthometallation, thereby incorporating deuterium into the phosphite ligand. In this sequence, **1** ⇌ **6** ⇌ **5** ⇌ **4**, one would expect the incorporation of deuterium into acac to be observed immediately, and the rate of this exchange to be as fast as, if not faster than, the rate of D-substitution into the phosphite ligand. However, this situation is not observed. The experimental results indicate that the rate of substitution of deuterium into acac is

slower than the incorporation of deuterium into $P(OPh)_3$. Therefore, the first step of the H/D exchange process must be the orthometallation of the triphenyl phosphite ligand, **1** → **2**. The reductive elimination of Hacac from the rhodium(III) center leads to the regeneration of a Rh(I) species, **3**. Deuterium is then incorporated into the triphenyl phosphite ligand via the oxidative addition of D_2, **3** → **4**, followed by reductive elimination of the aryl and deuterium ligands, **4** → **5**. For deuterium incorporation into acac to reflect the extent of deuteration of the $P(OPh)_3$ ligand, the source of deuterium for the acetylacetone ligand must be the ortho positions of the phosphite ligand. This may be provided by rapid and reversible interconversions between **5** and **4** in which the deuteride of **5** is scrambled among all of the ortho positions of $P(OPh)_3$, or it may be provided by the conversion of **1** to **2**. In any case, at 75°C there is no observable difference in the extent of deuteration of the two ligands, and the cycle of Scheme I is traversed smoothly. At 60°C, however, D-incorporation into acac proceeds more slowly than into $P(OPh)_3$, suggesting that interconversions of **5** ⇌ **4** ⇌ **3** occur more readily than the readdition of Hacac to the rhodium center either **5** → **6** or **3** → **2**. This readdition is required in order to obtain deuterium incorporation into the methine position of the acetylacetonate ligand via **5** ⇌ **6** or **1** ⇌ **2** ⇌ **3**.

In the H/D exchange acetylacetone may remain weakly bound to the rhodium center as suggested in Scheme I, or it may dissociate entirely from the metal center. If Hacac were to remain weakly coordinated, then it would be expected to adopt coordination mode I or II as shown below. If Hacac were totally dissociated from Rh, then it would be expected to bind to the metal center via I or II prior to the



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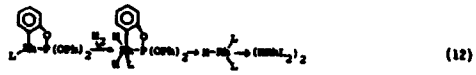
formation of the acac chelate ring. For D-incorporation into acac, there must occur the formation of either weakly coordinated or free Hacac which can achieve H/D exchange via keto-enol tautomerism. The observation of a small amount of free acetylacetone by ^{1}H NMR spectroscopy when $P(OPh)_3$ is added to the reaction solution (reaction 2 of Table I) shows that complete dissociation of Hacac is occurring to a limited extent.

The observation that Hacac can be reductively eliminated from the rhodium center is very important because of the interest in rhodium acetylacetonate complexes as homogeneous catalyst precursors. The loss of the acac ligand from rhodium has been observed previously but under more severe conditions (eg. 40 atm 1:1:1 $CO/H_2/C_2H_4$ for $Rh(CO)_2(acac)$[3]). We have shown that the reductive elimination of Hacac (or Dacac) from $Rh(P(OPh)_3)_2(acac)$ occurs under relatively mild conditions (60°C, 360 torr H_2). In a metal acac complex, the acac ligand is a formal 3e-donor, therefore the reductive elimination of Hacac and subsequent dissociation from the metal center reduces the electron count of the metal center by 4. The loss of this bidentate ligand via reductive elimination and dissociation therefore generates a high degree of coordinative unsaturation at the rhodium center. The ease of this ligand displacement may explain the usefulness of complexes of this type as catalyst precursors. The dissociation of Hacac from species 1 in Scheme I generates a highly unsaturated three-coordinate Rh(I) complex 7. A complex of this type may be involved in the hydrogenation of arenes recently reported to be catalyzed by complex 1 under 10 atm of H_2 at 80°C. Similar rhodium phosphite complexes of the type $[(L)Rh[P(O\text{-}i\text{-}Pr)_3]_2]_2$ are known to be exceptionally active catalyst precursors for olefin hydrogenation reactions.[12] The rhodium tri(isopropyl)phosphite dimer is closely related to species 7 in Scheme I by the proposed sequence of reactions shown in equation 12, where L = $P(OPh)_3$.



7 (12)

Thus, the catalytic activity of analogous rhodium acac complexes is most likely a result of the ease of acac displacement via Hacac reductive elimination and dissociation. A closer examination of other catalytic reactions involving Rh(acac) complexes as catalyst precursors will undoubtably support this conclusion.

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Table I. Conditions for H/D exchange reactions

		Reactants (μmol)			
Reaction	T (°C)	Complex 1	Hexene	$P(OPh)_3$	D_2
1	75	5.4	-	-	53[a]
2	75	6.0	-	6.0	52
3	75	3.6	9.8	-	53
4	75	6.0	3.0	6.0	51
5	60	2.4	-	-	56
6	60	3.0	-	-	38

[a] This corresponds to a D_2 pressure of 405 torr at 298°K

Table II. S-Deuterium incorporation into coordinated ligands at 60°C.

Reaction[a]	$t_{1/2}$ (hr)	S - D acac	S - D $P(OPh)_3$	k^c (sec^{-1})
5	0.6	3	14	9.6×10^{-5}
	1.4	3	38	
	3.0	5	46	
	6.6	7	92	
	20[b]	9	82	
6	0.3	3	6	6.1×10^{-5}
	1.1	3	21	
	4.1	5	28	
	5.9	8	31	
	9.1	23	38	
	16.3	40	98	
	38.0	84	87	

[a] Reaction conditions given in Table I. [b] After 6.6 hr reaction at 60°, the NMR tube is maintained at room temperature for the following 13.2 hr. [c] Rate constant k from equation (10) corresponding to initial deuteration.

Scheme I. Proposed mechanism for H/D exchange

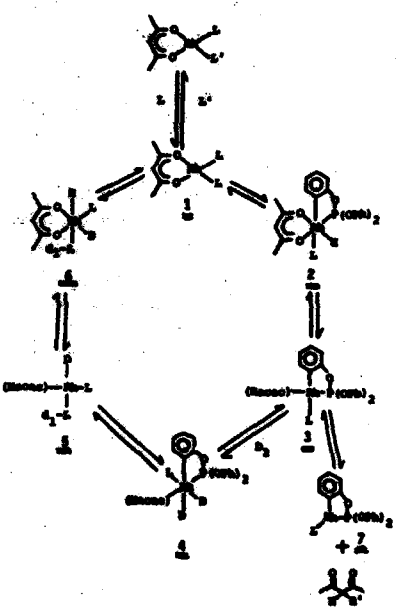
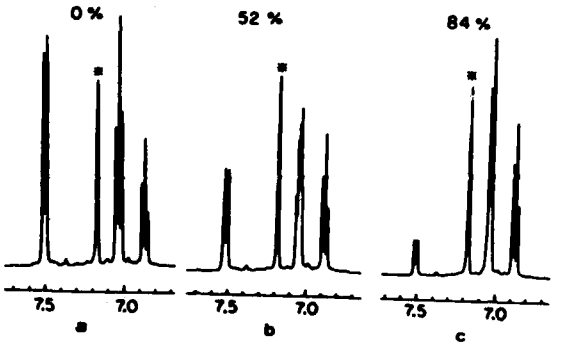
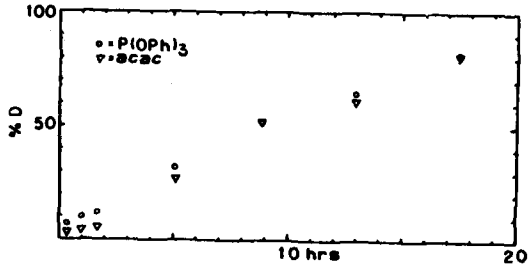


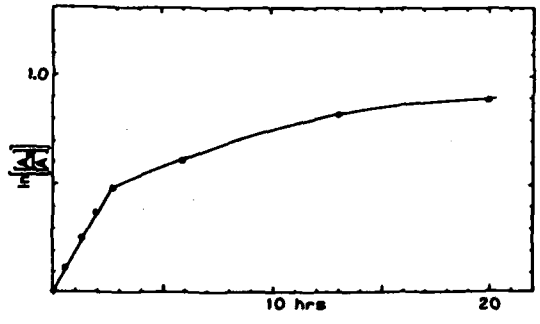
Figure 1: Aromatic regions of the 400-MHz ^1H NMR Spectra of Complex 1 under D_2. * = C_6H_6.

Figure 2: Plot of deuterium-incorporation into the $P(OPh)_3$ and acetylacetone ligands of complex 1 for reaction 1 (Table I.) vs. time.

Figure 3: Plot of ln ($[A_0]/[A]$) vs. time for reaction 5 (Table I).




100
50
% D
•: P(OPh)3
▽: acac
10 hrs
20


1.0
10 hrs
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