MNR groups are characterized by varied amounts of $M \leftarrow N$ π bonding, over and above the π character inherent in the minimal $M{=}N$ double bond.

To place the present work in context we may select from the literature two structures that represent, or at least tend toward, the limits. The key structural features for these compounds of rhenium[13] and molybdenum[14] are shown in Figure 2. The rhenium case is essentially at the limit of bond order 3 with its angle of 180°. Bearing in mind that the radius of the tungsten atom is 0.02 to 0.03 Å greater than that of the rhenium atom, we conclude that a full W—N bond would probably have a length of 1.71–1.72 Å. For the molybdenum compound the bond angle of 139.4° instead of 120° has been interpreted[14] to imply a bond order of about 2.3, and a distance of perhaps 1.84 Å suggested for a pure double bond. The observed angles (ca. 165°) and distances (1.74 Å) in the present case then are closer to the triple bond limit and suggest a bond order of about 2.8. This considerable, but incomplete, formation of the second π bond is consistent with our earlier analysis of the W–O bonding, where we drew the conclusion that the tungsten atoms receive a moderate amount of π electron density from the oxygen atoms to which they are bonded. However, the oxygen atoms alone only partially satisfy the capacity of the tungsten atom in this respect, and thus the RN group can compete effectively and make about three-quarters of its total possible contribution.

In a recent preliminary publication[15] the preparation and structure of the dinuclear compound $[(PhN)(MeO)_3W]_2(\mu\text{-}OMe)_2$ were reported. The structure is formed by two octahedra sharing an edge, and the $W\cdots W$ distance is given as 3.47 Å. Since there are only two OR bridges in this case, whereas in our compound there is also the bridging oxygen atom, the shorter distance, 3.06 Å, in our compound bears a reasonable relation to this one. The dimensions of this other compound are reported only partially and they have somewhat large esd's, so that further detailed comparison of the two structures would be of uncertain value. The pattern of W–O distances is comparable in the two cases, but the reported W–N distance, 1.65 (2) Å, is considerably shorter than ours. We can see no reason for such a marked difference, and we therefore look forward to a complete report of a fully refined structure to see whether the discrepancy will lessen.

We also note that a reaction in which $CpMo(CO)_2{\equiv}Mo(CO)_2Cp$ reacts with $PhNO_2$ to give a product containing μ_2-PhN and both μ_2-O and terminal O has been reported recently.[16]

Acknowledgment. We thank the National Science Foundation for support and Dr. B. L. Haymore for a helpful discussion.

Registry No. $[W(OCMe_3)_2(NPh)]_2(\mu\text{-}O)(\mu\text{-}OCMe_3)_2$, 89711-33-1; $W_2(OCMe_3)_6$, 57125-20-9; C_6H_5NO, 586-96-9.

Supplementary Material Available: Table of observed and calculated structure factors, anisotropic thermal parameters, and bond lengths and bond angles and a more detailed account of the crystallographic work (46 pages). Ordering information is given on any current masthead page.

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

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Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. *Received September 22, 1983*

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 75 °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 60 °C, deuterium incorporation into $P(OPh)_3$ is initially more rapid than that into the acac ligand. The initial rate of deuterium incorporation into $P(OPh)_3$ by **1** in benzene-d_6 under D_2 at 60 °C proceeds with a first-order rate constant of 9.6×10^{-5} s^{-1}. A mechanism for this exchange process is proposed.

Rhodium(I) complexes containing a single acetylacetonate (acac) ligand of the type RhLL′(acac) (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 Barefield and Parshall[7] and have been found to undergo H/D

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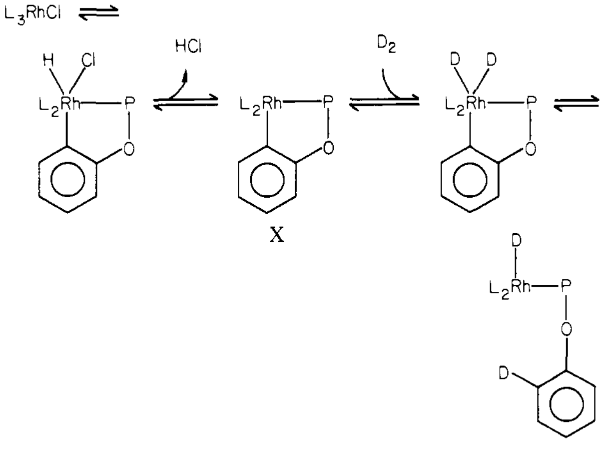
Table I. Conditions for H/D Exchange Reactions

reaction	T, °C	reactants, µmol complex 1	Hacac	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 495 torr at 298 K. Other entries in this column are calculated accordingly.

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-metalated intermediate X as shown in eq 1. On the basis of the reactivity of known rhodium(I) phosphite 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.



(1)

Experimental Section

Rh(P(OPh)$_3$)$_2$(acac) was prepared by the literature method.[8] All experiments were performed in sealed NMR tubes in benzene-d_6. ^{1}H NMR spectra were recorded on a Bruker WH-400 400-MHz instrument, with chemical shifts reported in ppm relative to Me$_4$Si.

General Procedure for ^{1}H 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 and P(OPh)$_3$)) and benzene-d_6 (0.5 mL) 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 ^{1}H 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 (95% deuterium incorporation), half of the benzene-d_6 solution of complex **1**-d_{13} (2.7 µmol) is treated with P(OPh)$_3$ (1.5 µL, 5.7 µmol), and its ^{1}H NMR spectrum is recorded immediately. The deuterium content of the ortho position of coordinated P(OPh)$_3$ is 46% within 5 min 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.

acac Exchange and Interligand H/D Exchange Reactions. Benzene-d_6 is distilled in vacuo into a 5-mm NMR tube containing Rh(P(OPh)$_3$)$_3$-(acac) (7.3 mg, 8.9 µmol), and the tube is flame sealed under D$_2$ (700 torr). The solution is then heated at 75 °C for 20 h. Analysis of the reaction mixture by ^{1}H NMR spectroscopy indicates 80% deuterium incorporation into the ortho positions of coordinated P(OPh)$_3$ and 77% deuterium incorporation into the methine position of acac. The NMR tube is broken open in air, and acetylacetone (7 µL, 68 µmol) is added to the reaction mixture, which is then shaken for 45 min. Solvent and excess acetylacetone are removed in vacuo, fresh benzene-d_6 is distilled into the NMR tube, and the tube is sealed under vacuum. ^{1}H NMR analysis indicates 80% deuterium content in P(OPh)$_3$ and 0% deuterium content in coordinated acac. The sample is heated at 75 °C and monitored by ^{1}H NMR spectroscopy. After 1.5 h the deuterium content in acac is 18%, and after 24 h of heating, the deuterium content of the methine position of acac has reached 75%. The ^{1}H NMR spectra for this experiment were recorded on a Bruker WM-250 250-MHz instrument.

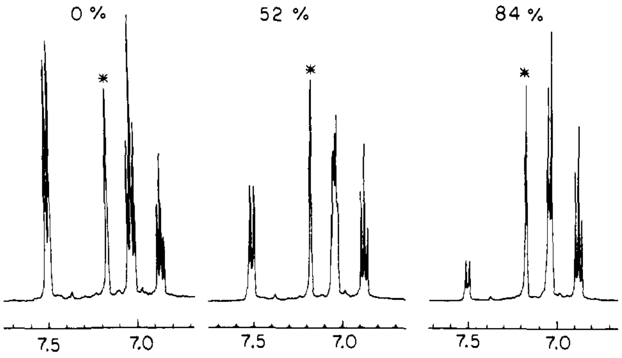


Figure 1. Aromatic regions of the 400-MHz ^{1}H NMR spectra of complex **1** under D$_2$ (asterisk represents C$_6$H$_6$).

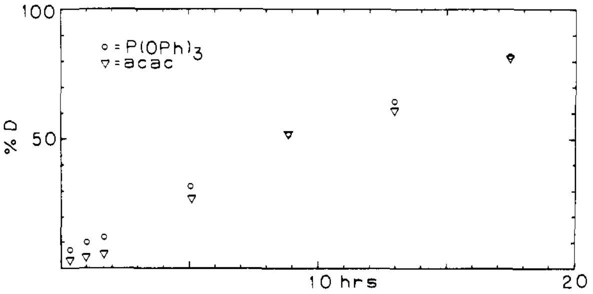


Figure 2. Plot of deuterium incorporation into the P(OPh)$_3$ and acetylacetone ligands of complex **1** for reaction 1 (Table I) vs. time.

Results and Discussion

H/D Exchange at 75 °C. When a benzene-d_6 solution of Rh(P(OPh)$_3$)$_2$(acac) (**1**) is heated at 75 °C under D$_2$ (495 torr) (reaction 1, Table I) a gradual change is observed in the 6.8–7.5 ppm region of its ^{1}H 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 7.48 ppm and are split into a doublet by the meta hydrogens ($J_{\text{o-m}}$ = 8.0 Hz). 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 ($J_{\text{m-p}}$ = 7.4 Hz). 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 hydrogen resonances (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 = 7.4 Hz). 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 rhodium(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

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[7] Barefield, E. K.; Parshall, G. W. *Inorg. Chem.* **1972**, *11*, 964.

[8] Trzeciak, A. M.; Ziōlkowski, J. J. *Inorg. Chim. Acta Lett.* **1982**, *64*, L267.

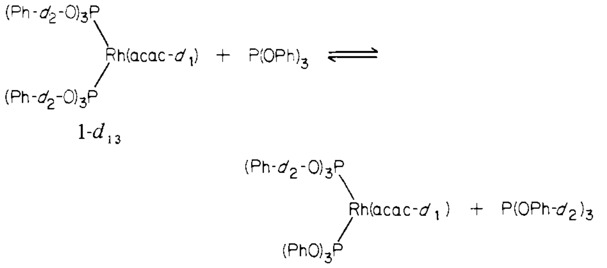
[9] Parshall, G. W.; Knoth, W. H.; Schunn, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 4990.

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 homologues. When the reaction is carried out in benzene-d_6 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. In addition, the reaction in benzene-d_6 under H_2 shows that D_2, and not deuterated solvent, serves as the ultimate deuterium source; no evidence for H/D exchange is observed in this experiment nor is there an increase in the resonance corresponding to benzene-d_5.

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, i.e., 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 ortho-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 of $P(OPh)_3$, 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 of $P(OPh)_3$ and 0.5 equiv of 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 equiv of $P(OPh)_3$ is added to the benzene-d_6 solution of **1**-d_{13} (95%, 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 5 min, the integrated intensity of the ortho protons from coordinated $P(OPh)_3$ indicates a 46% deuterium content, which corresponds to complete scrambling of labeled and unlabeled $P(OPh)_3$ ligands (eq 2a).



$$[(\text{Ph-}d_2\text{-O})_3\text{P}]_2\text{Rh(acac-}d_1) + \text{P(OPh)}_3 \rightleftharpoons (\text{Ph-}d_2\text{-O})_3\text{P}(\text{PhO})_3\text{P}\text{Rh(acac-}d_1) + \text{P(OPh-}d_2)_3 \quad (2a)$$

1-d_{13}

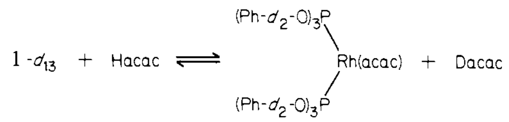
The facile exchange of free and coordinated phosphite ligands in this system contrasts with a recent study using ^{31}P NMR spectroscopy which concludes that phosphite exchange for **1** does not occur or occurs only very slowly. While this ligand exchange may be too slow to be observed by room-temperature NMR line broadening, it is readily observed at room temperature using labeled 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.

Table II. Percent Deuterium Incorporation into Coordinated Ligands at 60 °C

		% D		
reaction[a]	time, h	acac	$P(OPh)_3$	k,[c] s^{-1}
5	0.5	3	14	9.6×10^{-5}
	1.4	3	38	
	3.0	5	45	
	6.6	7	52	
	20[b]	9	52	
6	0.3	3	6	6.1×10^{-5}
	1.1	3	21	
	4.1	5	28	
	5.9	8	31	
	9.1	33	38	
	16.3	40	58	
	38.0	84	87	

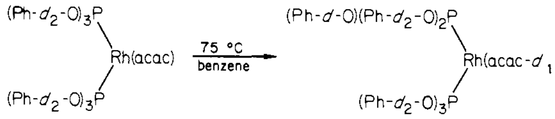
[a] Reaction conditions given in Table I. [b] After 6.6-h reaction at 60 °C, the NMR tube is maintained at room temperature for the following 13.2 h. [c] Rate constant k from eq 10 corresponding to initial deuteration.

Exchange involving free and coordinated acac also occurs easily, as seen by taking a sample of deuterated **1** (80% labeled), adding 7.6 equiv of Hacac, and shaking the resultant solution at room temperature for 45 min. Isolation and characterization of the complex show that while the ortho phenyl positions of $P(OPh)_3$ remain 80% deuterated, the methine position of acac is fully protiated, indicating that acac exchange has taken place (eq 2b).



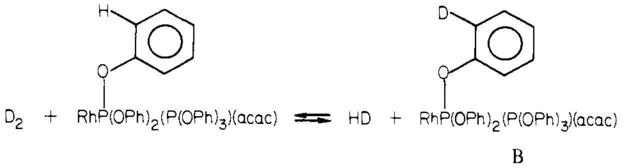
$$1\text{-}d_{13} + \text{Hacac} \rightleftharpoons [(\text{Ph-}d_2\text{-O})_3\text{P}]_2\text{Rh(acac)} + \text{Dacac} \quad (2b)$$

When this complex, deuterated at phosphite and protiated at acac, is dissolved in benzene, sealed under vacuum in an NMR tube, and heated at 75 °C, it is observed that the methine position of acac becomes deuterated as shown in eq 2c (18% after 1.5 h; 75% after 24 h). The phosphite ligand thus serves as a deuterium source for H/D exchange into acac.



$$[(\text{Ph-}d_2\text{-O})_3\text{P}]_2\text{Rh(acac)} \xrightarrow[\text{benzene}]{75\ ^\circ\text{C}} (\text{Ph-}d\text{-O})(\text{Ph-}d_2\text{-O})_2\text{P}(\text{Ph-}d_2\text{-O})_3\text{P}\text{Rh(acac-}d_1) \quad (2c)$$

H/D Exchange at 60 °C. 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 eq 3, can be considered a simple isotope exchange reaction, which is the first of a series of H/D exchanges of the general form **1**-d_x + D_2 ⇄ **1**-d_{x+1} + HD, where x = 0–12. However, as the exchange process continues, the kinetics of H/D



B

(3)

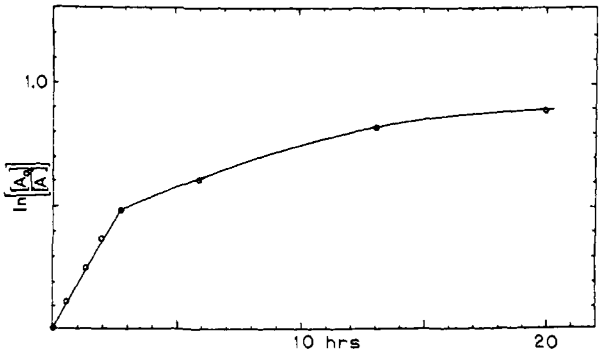


Figure 3. Plot of ln ($[A_0]/[A]$) vs. time for reaction 5 (Table I).

exchange grows in complexity due to the increasing probability of back-reactions and degenerate exchanges as shown in eq 4–9.

back-reactions

$$(D_x)\text{-}\mathbf{1} + HhD \rightleftarrows (D_{x-1})\text{-}\mathbf{1} + D_2 \qquad (4)$$

$$(D_x)\text{-}\mathbf{1} + H_2 \rightleftarrows (D_{x-1})\text{-}\mathbf{1} + HD \qquad (5)$$

degenerate exchange

$$(D_xD^*)\text{-}\mathbf{1} + D_2 \rightleftarrows (D_xD)\text{-}\mathbf{1} + DD^* \qquad (6)$$

$$(D_xD^*)\text{-}\mathbf{1} + HD \rightleftarrows (D_xD)\text{-}\mathbf{1} + HD^* \qquad (7)$$

$$(D_xH^*)\text{-}\mathbf{1} + HD \rightleftarrows (D_xH)\text{-}\mathbf{1} + H^*D \qquad (8)$$

$$(D_xH^*)\text{-}\mathbf{1} + H_2 \rightleftarrows (D_xH)\text{-}\mathbf{1} + HH^* \qquad (9)$$

After several exchanges have occurred, there 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 ^1H NMR spectroscopy. A 1:1:1 triplet ($J = 42$ Hz) at 4.42 ppm is seen for HD, while H_2 gives rise to a singlet at 4.46 ppm (in benzene-d_6). 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 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, **1**. For example, in reaction 5 (Table I) under 517-torr pressure the concentration of D_2 in solution is roughly 3 mM while the concentration of **1** is 4.8 mM. 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 **1** + D_2 can be obtained by using eq 10 derived by Calvin[10] and other workers,[11] which deals with the rate of single isotope exchange. $[A_0]$ is the concentration of A at $t = 0$, $a = [D_2] + [HD]$, $b = [A] + [B]$, and

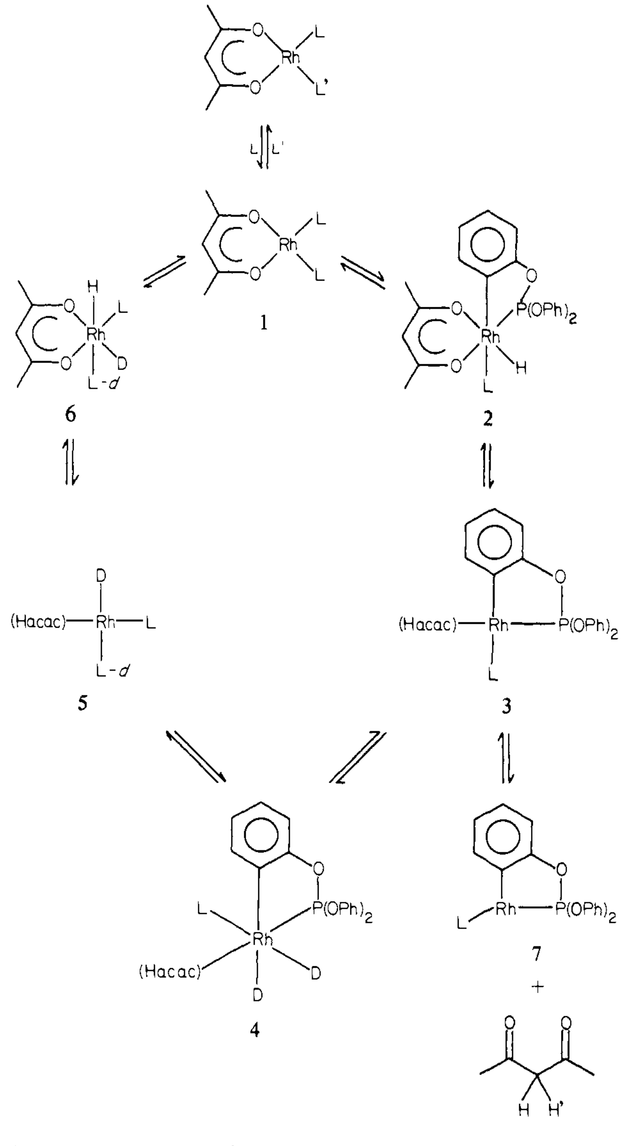
$$\ln \frac{[A_0]}{[A]} = \frac{R}{ab}(a + b)t = kt \qquad (10)$$

A and B are defined in eq 3. A plot of ln ($[A_0]/[A]$) vs. t for reaction 5, shown in Figure 3, is linear durign the initial stages of the reaction and yields a value for k in eq 10 of 9.6×10^{-5} s^{-1}.

Mechanism of H/D Exchange

Any mechanism drawn for the H/D exchange reactions of complex **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 and acetylacetone; (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 75 °C; (5) at 60 °C, the rate of deuteration of $P(OPh)_3$ is faster than that of acac; (6) during the reaction of **1** with D_2 or H_2, no species except for **1** is detected by ^1H NMR spectroscopy; (7) during the reaction of **1** with D_2 in the presence of excess $P(OPh)_3$, free acetylacetone is observed by ^1H NMR; and (8) under vacuum, deuterated phosphite is observed to serve as the deuterium source for H/D exchange into acac. These facts lead us to the proposed mechanism for H/D exchange which is shown in Scheme I.

Scheme I. Proposed Mechanism for H/D Exchange



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 eq 11.[12] Following the first

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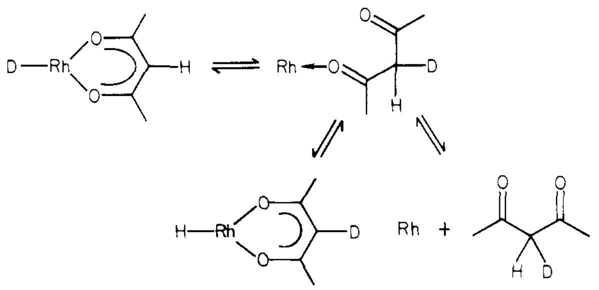
(10) Duffield, R. B.; Calvin, M. *J. Am. Chem. Soc.* **1946**, *68*, 557.

(11) Moore, J. W.; Pearson, R. G. "Kinetics and Mechanism"; Wiley: New York, 1981; p 311 and references therein.

(12) The possibility of acac H/D exchange in this system proceeding by an acid–base mechanism involving H^+/D^+ is unlikely because of the anhydrous reaction conditions employed and the generally nonacidic nature of Rh hydrides.

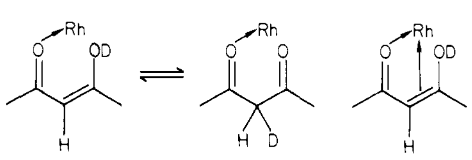


(11)

oxidative addition, which is either that of D_2 or of the orthophenyl 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 eq 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 ortho metalation of the phosphite ligand to the rhodium(I) center.

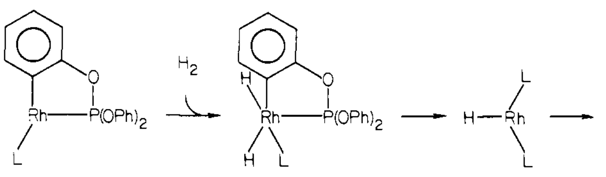
If the oxidative addition of D_2 to complex **1** were to occur first, then one forms species **6** having two deuteride ligands. The reductive elimination of Dacac from **6** yields species **5**, which can then undergo reversible ortho metallation, thereby incorporating deuterium into the phosphite ligand. In this sequence, $\mathbf{1} \rightleftarrows \mathbf{6} \rightleftarrows \mathbf{5} \rightleftarrows \mathbf{4}$, 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 ortho metalation of the triphenyl phosphite ligand, $\mathbf{1} \rightarrow \mathbf{2}$. The reductive elimination of Hacac from the Rh(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, $\mathbf{3} \rightarrow \mathbf{4}$, followed by reductive elimination of the aryl and deuterium ligands, $\mathbf{4} \rightarrow \mathbf{5}$. 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 $\mathbf{5} \rightleftarrows \mathbf{4} \rightleftarrows \mathbf{3}$ occur more readily than the readdition of Hacac to the rhodium center either $\mathbf{5} \rightarrow \mathbf{1}$ or $\mathbf{3} \rightarrow \mathbf{2}$. This readdition is required in order to obtain deuterium incorporation into the methine position of the acetylacetonate ligand via $\mathbf{5} \rightleftarrows \mathbf{6}$ or $\mathbf{1} \rightleftarrows \mathbf{2} \rightleftarrows \mathbf{3}$.

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. 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 formation of the acac chelate ring. For D incorporation into acac, there must occur the formation of either weakly coordinated or free Dacac, which can achieve H/D exchange via keto-enol tautomerism. The observation of a small amount of free acetylacetone by ^1H 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.



I II

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 (e.g., 40 atm of 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, 350 torr of D_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 four. 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 **3** 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 $\{HRh[P(O\text{-}i\text{-}Pr)_3]_2\}_2$ are known to be exceptionally active catalyst precursors for olefin hydrogenation reactions.[13] The rhodium triisopropyl phosphite dimer is closely related to species **7** in Scheme I by the proposed sequence of reactions shown in eq 12, where L = $P(OPh)_3$. 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 undoubtedly support this conclusion.



7

$(HRhL_2)_2$ (12)

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Registry No. 1, 25966-19-2; D_2, 7782-39-0.

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