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TRANSITION METAL ACTIVATION AND FUNCTIONALIZATION OF CARBON-HYDROGEN BONDS

PROGRESS REPORT

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ABSTRACT

This project is directed towards the continued investigation of the fundamental thermodynamic and kinetic factors that influence carbon-hydrogen bond activation at homogeneous transition metal centers. The project is also directed towards the conversion of hydrocarbons into functionalized products of potential use to chemical industry. Our goals during the grant period will be 1) to identify new transition metal complexes capable of activating arene and alkane C-H bonds, 2) to quantitatively evaluate the kinetic and thermodynamic stability of these complexes, and 3) to examine routes for functionalization of the activated hydrocarbons. These studies will also contribute towards the formulation of a unified theory of C-H bond activation that applies to other transition metal complexes.

The specific complexes involved in these studies are derivatives of the formulation $(C_5Me_5)Rh(PR_3)(R)H$, $Fe(PMe_3)_2(CNR)_3$, $Ru(PR_3)_4(R)H$, and $Rh(CNR)_3H$. Functionalization will focus upon isocyanide and acetylene insertion reactions. New compounds that activate hydrocarbon C-H bonds include $HRe(PR_3)_5$, $HRe(PR_3)_2(CNR)_3$, $CpRe(PR_3)H_4$, $CpRe(PR_3)_2H_2$, $(\eta^6\text{-}C_6H_6)Re(PPh_3)_2H$, and $MnH_3(dmpe)_2$. The latter complex is found to be an η^2-dihydrogen complex. The new complexes $RhCl[P(i\text{-}Pr)_3]_2(CNCH_2CMe_3)$ and (trispyrazolylborate)$Rh(CNR)_2$ are shown to be active for the activation and functionalization of aromatic C-H bonds.

In the third year of this project, significant advances have been made in the observation of η^2-arene complexes of $[(C_5Me_5)Rh(PMe_3)]$. The complex $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-phenanthrene})$ has been structurally characterized. Several other η^2-complexes have also been prepared.

A. Previous Studies Under DOE Contract - Year Three.

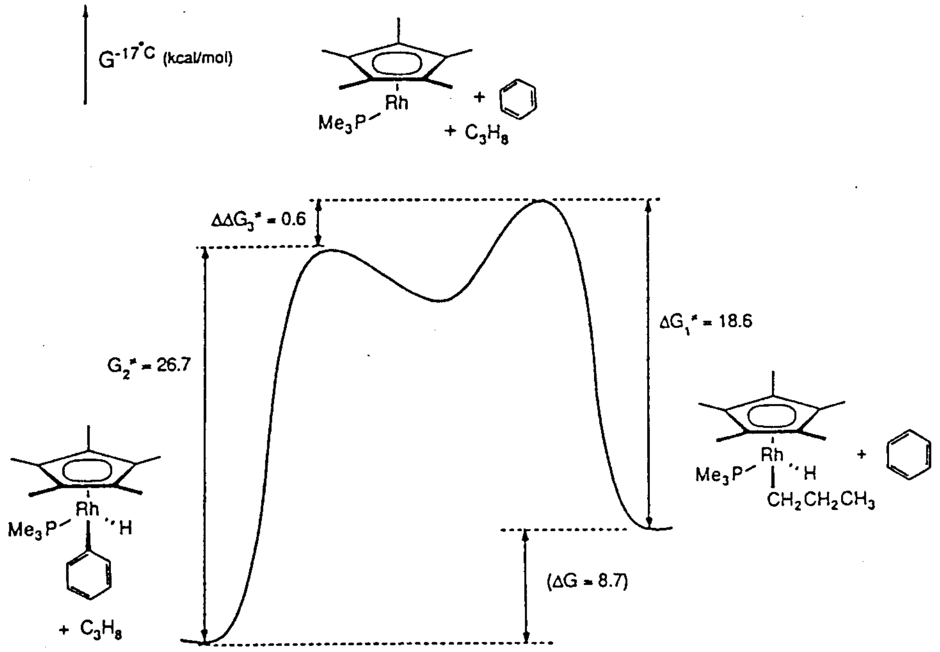
A.1. Intermolecular Arene and Alkane Activation.

The complexes initially chosen for study, $(C_5Me_5)Rh(PMe_3)(R)H$, employ features commonly found in molecules that were known to activate C-H bonds (the presence of electron donating ligands, the availability of a $2e^-$ redox couple). This system was the first to permit examination of both alkane and arene C-H bond oxidative addition and reductive elimination by the exact same metal complex, and has provided a wealth of kinetic and thermodynamic information. This work has been succinctly summarized in a recent article in Acc. Chem. Res.,[1] and our first full paper on these studies was recently reported to be one of the 100 most cited articles in chemistry in 1984.[2]

Whereas the alkyl derivatives all displayed first order kinetics for irreversible reductive elimination of alkane at or about -20°C, the aryl complexes did not undergo reversible reductive elimination until about 60°C. The intermediate responsible for C-H activation is believed to be the 16-electron transient species $[(C_5Me_5)Rh(PMe_3)]$, which can also be generated at low temperatures by irradiation of $(C_5Me_5)Rh(PMe_3)H_2$. Irradiation of the dihydride in liquid propane at -55°C produces the propyl hydride complex $(C_5Me_5)Rh(PMe_3)(CH_2CH_2CH_3)H$, affording one of the first examples of alkane oxidative addition to a transition metal center. Irradiation of the dihydride in a mixed solvent, propane/benzene, shows only a slight kinetic preference for benzene (4:1) over propane, despite the overwhelming thermodynamic preference, as summarized in Scheme I.

The aryl hydride complexes $(C_5Me_5)Rh(PMe_3)(Aryl)H$ were all proposed to be in rapid equilibrium with the less stable η^2-arene complexes $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-Arene})$. Evidence for this equilibration process included: (1) the direct observation of the isomerization of a p-tolyl aryl group to a m-tolyl aryl group in $(C_5Me_5)Rh(PMe_3)(tolyl)H$ at low temperature, (2) spin

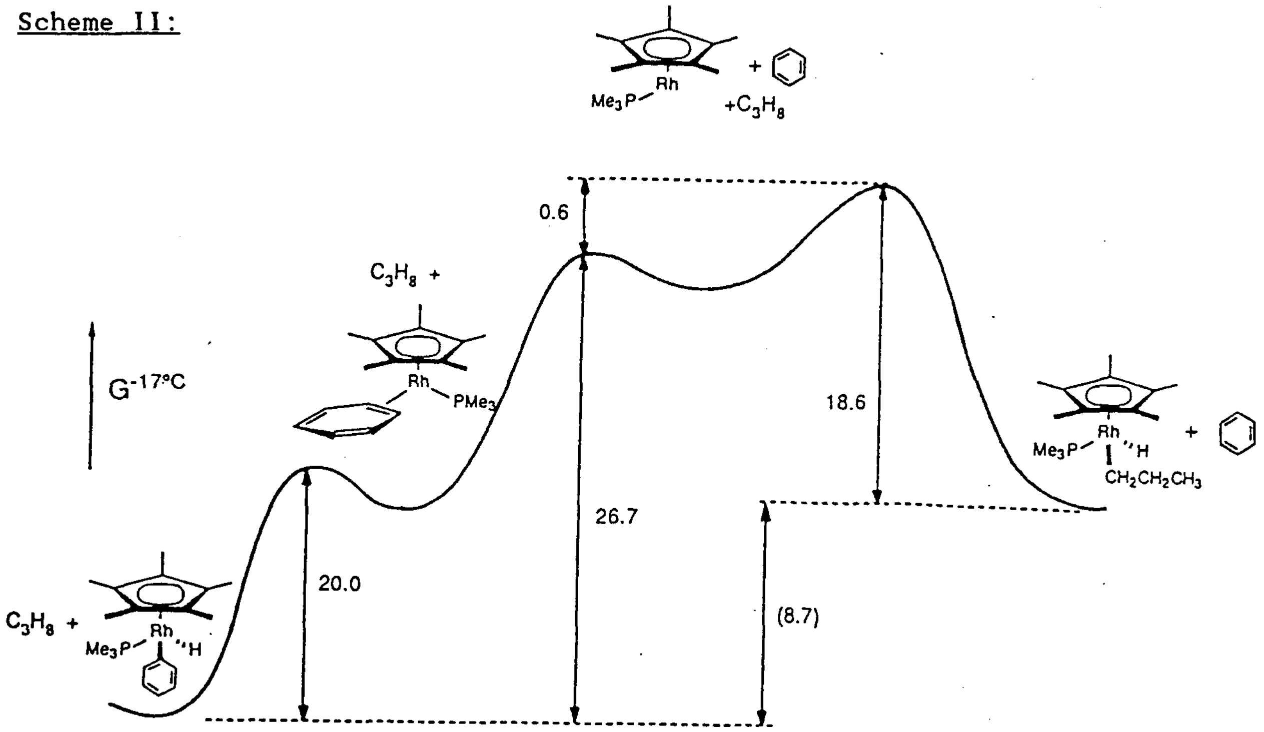
Scheme I:



saturation transfer between the distinct methyl groups of the p-xylyl aryl group in $(C_5Me_5)Rh(PMe_3)(2,5\text{-}C_6H_3Me_2)H$, (3) the isomerization of $(C_5Me_5)Rh(PMe_3)(C_6D_5)H$ at -10°C, which shows a stepwise [1,2] migration of the proton from the metal to the ortho position of the phenyl ring followed by migration to the meta and para positions. In all cases, the reductive elimination of arene from $(C_5Me_5)Rh(PMe_3)(Aryl)H$ occurs at -10°C, about the same temperature as that for the alkyl hydride complexes. The greater macroscopic stability of the aryl complexes results from the coordination of the arene in an η^2 fashion in the transition state for reductive elimination. Additional energy must be supplied in order to break the η^2-arene-metal interaction (Scheme II).

The above studies and the postulated intermediacy of η^2-arene complexes offered a chemically sensible way to account for the observed thermodynamic and kinetic selectivities. However, the η^2-arene complex was never observed with simple arenes such as benzene. Isotope effect studies were found to prove that an intermediate must be involved in arene activation, and the magnitude of these isotope effects is consistent with an intermediate having

Scheme II:

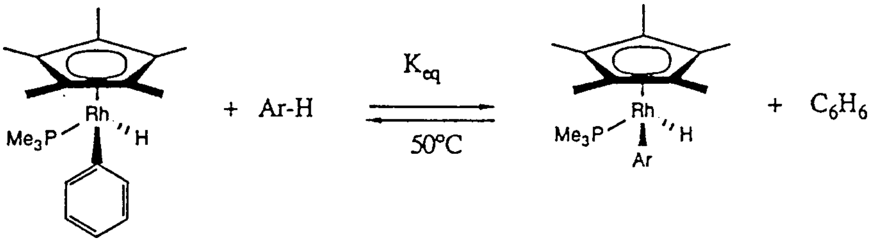


the η^2-arene structure.[3]

Very recently, continuation of the studies of the thermodynamic and kinetic selectivity by $[(C_5Me_5)Rh(PMe_3)]$ for different hydrocarbon substrates has led to new discoveries regarding the importance of η^2-arene coordination in C-H bond activation. Thermal exchange of $(C_5Me_5)Rh(PMe_3)(Ph)H$ (50 °C) with a variety of different arenes has been carried out for the purpose of determining equilibrium constants as a function of functional group and for determining positional selectivity. The results with m-xylene, toluene, anisole, mesitylene, and naphthalene are shown in Table I below. The preference for electron deficient arenes can be clearly seen.

As shown in the table, the reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with naphthalene was initially believed to give only the β-naphthyl isomer. In fact, further examination of this reaction has shown that another product is formed in even greater yield. (The product escaped initial identification as it contains no hydride resonance in the ^1H NMR spectrum.) ^{31}P NMR and 2D ^1H NMR (COSY, J-resolved spectroscopy) have proven invaluable for making

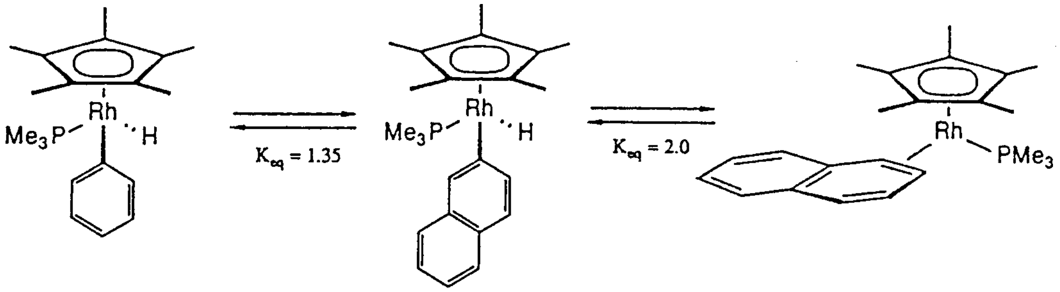
Table I.



Ar-H	K_{eq}	Positional Isomers
toluene	0.32	2:1 meta:para
o-xylene	0.13	100 % 3,4-xylyl
m-xylene	0.062	100% 3,5-xylyl
p-xylene	0.017	100% 2,5-xylyl
anisole	0.32	10:1.5:1 meta:para:ortho
mesitylene	0	-
naphthalene	1.35	"100%" 2-naphthyl

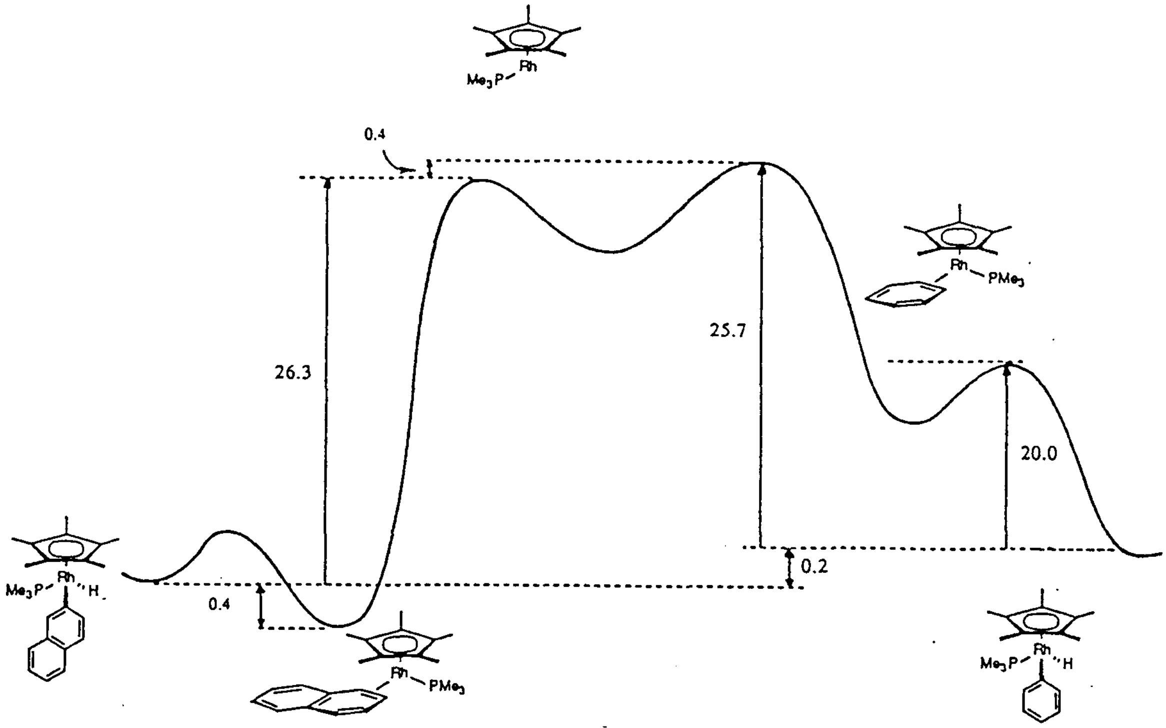
spectral assignments. The telling experiment was carried out by the thermal equilibration of $(C_5Me_5)Rh(PMe_3)(Ph)H$ in a hexane solution containing a 1:1 ratio of benzene and naphthalene. The β-naphthyl hydride complex is obtained in preference to the phenyl hydride complex under these conditions of thermodynamic control, but the major species in the solution turns out to be nothing other than *the η^2-naphthalene complex shown below* (Eq 1). Under conditions of thermal equilibrium, the η^2-arene complex is the preferred product![4]

Equilibria with 1:1 Benzene:Naphthalene in hexane solvent:



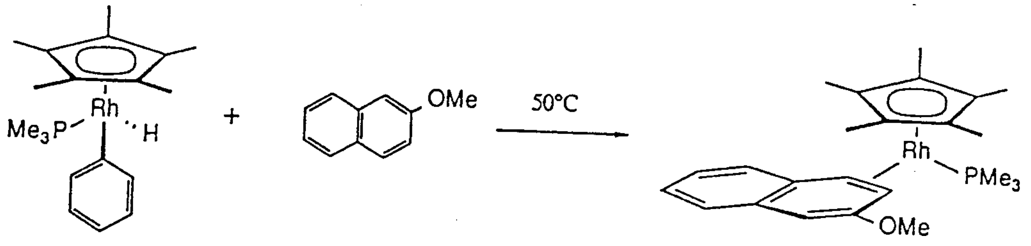
[1]

Scheme III.



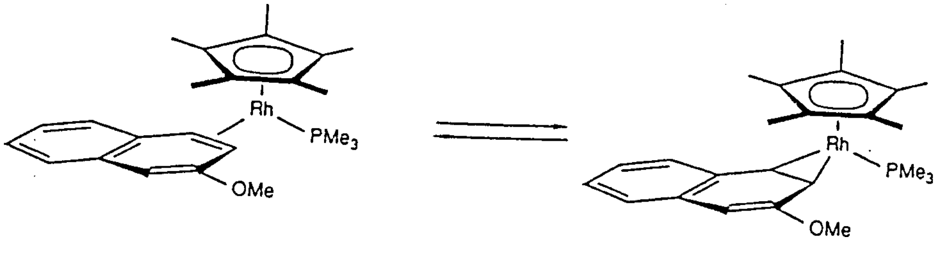
From the first order rate constant at which the naphthyl hydride complex undergoes reductive elimination of naphthalene, the free energy of activation can be calculated and combined with the equilibrium data and benzene data to yield the free energy picture shown in Scheme III. These data allow the calculation of the kinetic selectivity for benzene vs. naphthalene activation. The results provide the unexpected result that the thermodynamically less preferred arene benzene is kinetically preferred over naphthalene by a factor of over 2:1. Furthermore, the principle difference between benzene and the fused polycyclic aromatic naphthalene lies not in the stability of the aryl hydride complex, but rather in the stability of the η^2-arene complex. (It should be pointed out that the actual free energy of $(C_5Me_5)Rh(PMe_3)(\eta^2$-benzene) is not yet known, but must lie >3 Kcal/mole above the phenyl hydride complex since it is not observable, i.e. <1%, by NMR spectroscopy.)[4]

But why should naphthalene form such a stable η^2-complex? We have begun to search for the answer to this fundamental question by examining other fused polycyclic aromatics. One aromatic that we have examined so far might give a clue as to the answer. Upon heating a solution of $(C_5Me_5)Rh(PMe_3)(Ph)H$ in the presence of 2-methoxynaphthalene, a single product is formed in which η^2-complexation is completely favored over C-H activation (Eq 2). The energetics of activation/η^2-complexation have been reversed![4]



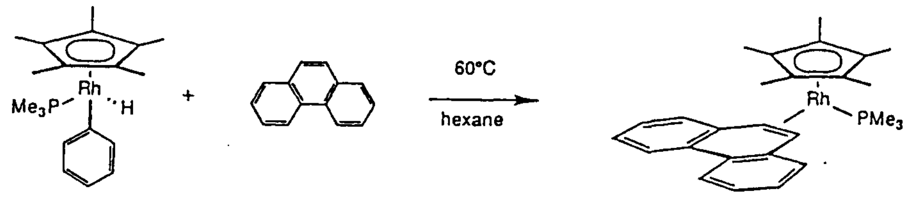
[2]

One explanation for the greater stability of this particular η^2-complex over an aryl hydride or other η^2-complex can be made after examination of the Dewar-Chatt-Duncanson model for olefin coordination (Eq 3). In the representation shown at the right, a styrene residue remains in which there is substantial resonance stabilization. The delocalization of an electron pair on the donor methoxy group provides even further stabilization compared to other isomers. Further studies are needed to fully evaluate the factors that lead to the preference for η^2-bonding in these special aromatics.



[3]

One other arene that we have examined also provides information about the nature of the η^2-interaction. Heating a solution of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with phenanthrene also gives only one product: a symmetrically bound η^2 complex (Eq 4). Furthermore, it has been possible after some effort to grow crystals



[4]

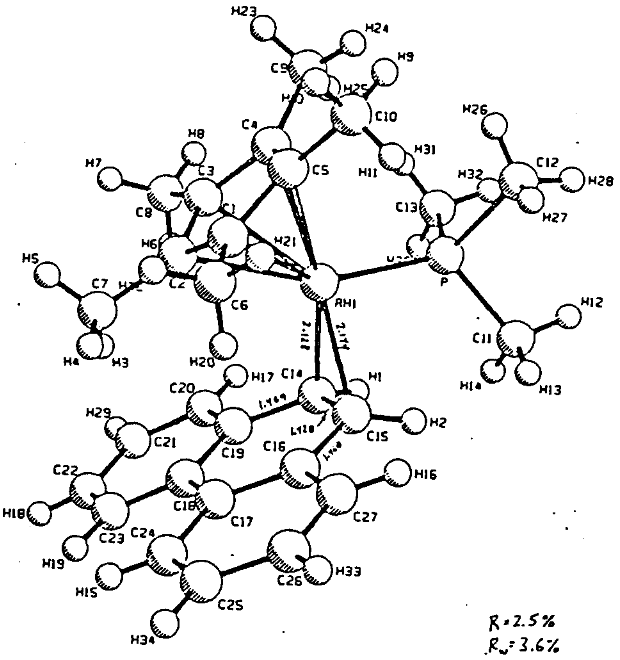
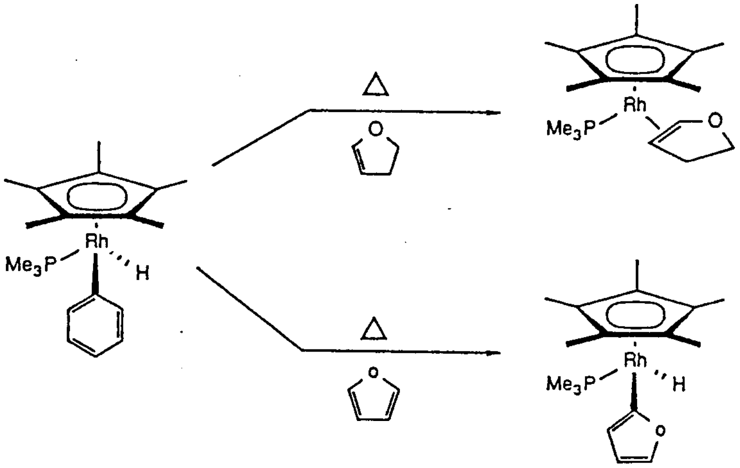


Fig. 1. ORTEP plot of $(C_5Me_5)Rh(PMe_3)(\eta^2\text{-phenanthrene})$.

and obtain a single crystal x-ray structure of this complex. Fig. 1 shows an ORTEP plot of the molecule with a symmetrically bound phenanthrene group.[4]

The above discoveries certainly re-open our active interest in pursuing the importance of η^2-arene complexes in C-H activation. Many questions about stability, kinetic and thermodynamic selectivity, and chemical reactivity will be examined in the next grant period, as described below. These molecules will offer a unique opportunity to examine why η^2-complexation occurs in some cases, and C-H activation occurs in others, a question that is currently of great interest in light of the many examples of olefin C-H bond activation rather than coordination.[5]

In reactions employing THF as solvent and no added arene, a side product was observed showing olefinic resonances (δ 2.42, dd, 1H; 3.94, d, 1H; 3.96, t, 1H; 5.76, m, 1H) as well as Cp* and PMe_3 resonances (δ 1.743, d, 15H; 0.979, d, 9H). Likely candidates for the product are dihydrofuran and furan complexes of Rh(I). Independent reactions of these organic ligands show yet different products, as summarized below (Eq 5). Thermolysis of $(C_5Me_5)Rh(PMe_3)(Ph)H$ in the presence of dihydrofuran gives an η^2-C_4H_6O complex, whereas thermolysis in the presence of furan gives the α-furanyl hydride adduct in which C-H bond activation has occurred! The aromaticity of the furan ring induces reactivity similar to an arene. This type of addition has not been seen before in the literature. The nature of the product from reaction with THF might involve ring-opening, and is under further investigation.



[5]

An attempt to synthesize the corresponding α-derivative failed in that reaction of α-naphthylmagnesiumbromide with $(C_5Me_5)Rh(PMe_3)Br_2$ gave the β isomer $(C_5Me_5)Rh(PMe_3)$(β-naphthyl)Br! This unprecedented rearrangement was most unexpected and is the subject of current investigation. Possible mechanisms for the rearrangement involve benzyne intermediates.

A.2. Intra- vs. Intermolecular Activation.

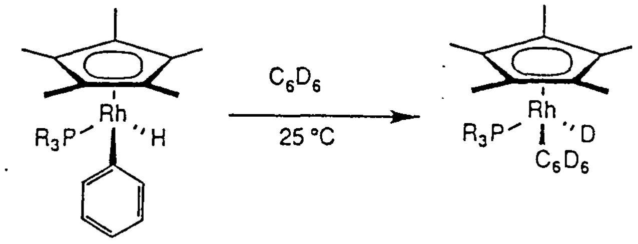
One fundamental problem in C-H bond activation that remains to be answered involves the factors that control competitive cyclometallation of ligands such as PMe_3 and C_5Me_5. We are currently evaluating the effects of phosphine chain length upon the selectivity for intramolecular vs intermolecular reaction, and have begun to investigate these effects with the more stable arene complexes.

Our initial intramolecular studies involved the activation of a C-H bond in the coordinated phosphine ligands $PMe_2CH_2C_6H_5$ and $PMe_2CH_2CH_2CH_3$. These cyclizations all involve formation of unstrained 5-membered rings where entropy changes associated with the closure of large rings is not a factor. The results led to the surprising conclusion that there is little kinetic preference for intramolecular reaction to make a 5-membered ring vs intermolecular reaction involving neat solvent, but that thermodynamically the intramolecular reaction is favored. Other phosphine ligands that can form 3-, 4- or 6-membered rings might show drastically different effects,[6] and were the targets of the next studies.

The complex $(C_5Me_5)Rh(PMe_2Ph)H_2$ has been prepared and irradiated in benzene solution. Only one product was observed and was identified as $(C_5Me_5)Rh(PMe_2Ph)(Ph)H$ by independent synthesis. Apparently, the phenyl group does not undergo competitive orthometallation. Irradiation of this complex in $c\text{-}C_6D_{12}$ does, however, result in formation of metallocycle. Furthermore, thermolysis of the complex $(C_5Me_5)Rh(PMe_2Ph)(Ph)H$ in C_6D_6 results in the formation of $(C_5Me_5)Rh(PMe_2Ph)(C_6D_5)D$, indicating that the arene is labile. However, thermolysis of the same material in $c\text{-}C_6D_{12}$ shows no apparent reaction. These observations indicate a strong thermodynamic and kinetic disfavoring of intramolecular orthometallation in the intermediate species $[(C_5Me_5)Rh(PMe_2Ph)]$.[7]

The investigation of other phosphine ligands has revealed some interesting new features. Table II below shows how phosphines effect the rate of benzene reductive elimination from $(C_5Me_5)Rh(PR_3)(Ph)H$. As can be seen, increasing steric bulk of the phosphine in the series $PMe_{3-x}Ph_x$ increases the arene lability. However, comparison of other entries with similar steric bulk

Table II.



PR_3	Cone Angle	$t_{1/2}$	ΔG^{*}
PMe_3	118	2 mos.	26.95
PMe_2Ph	122	64 hrs.	25.09
$PMePh_2$	136	19 hrs.	24.36
PPh_3	145	<30 min.	22.17
PMe_2Bu^t	123	20 days	26.30
PBu^n_3	132	105 hrs.	25.38

(PMe_2Bu^t, PBu^n_3) indicates that the electron withdrawing power of the phenyl groups is responsible for a great deal of the effect. In benzene solvent, there is no evidence for competitive intramolecular C-H bond activation with any of these ligands. Only with PMe_2Ph is there any indication of intramolecular activation as mentioned above.

Our work in this area has progressed in examining the relative importance of electronic and steric factors in driving the intramolecular oxidative addition reactions. The studies in Table II show that both cone angle and electron withdrawing groups on the phosphine accelerate the rate of reductive elimination of arene from $(C_5Me_5)Rh(PR_3)(Ph)H$ complexes.

Our systematic studies on the steric effects in these systems has involved the examination of the crystal structures of a series of these complexes, $(C_5Me_5)Rh(PPh_xMe_{3-x})(Ph)Br$. The relevant bond angles that form the tetrahedron at rhodium and the Rh-phenyl bond distances are shown in Table III. It can be seen that as the phosphine becomes larger, there is no obvious trend involving angles with the PR_3 group. However, the Rh-phosphorus bond distances are seen to increase significantly. The Rh-phenyl bond is also seen to lengthen in all of the complexes containing a phenyl group in the PR_3 ligand, confirming the weakening of this bond.[7] These effects can be partially interpreted in terms of simple VSEPR theory.

The weakening of the Rh-phenyl bond implies that the increased lability of arene in the PPh_3 complex relative to the PMe_3 complex can be directly attributed to a ground state destabilization of the oxidative addition adduct. On the other hand, the presence of electron donor groups on the phosphine probably effect the energetics of the transition state and the 16-electron intermediate more than the ground state oxidative addition adduct.

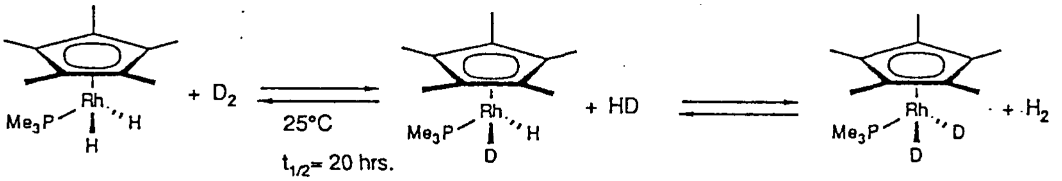
Table III. Central Bond Angles in the Complexes $(C_5Me_5)Rh(PPh_xMe_{3-x})(Ph)Br$.

	PMe_3	PMe_2Ph	$PMePh_2$	PPh_3
Cone angle of PR_3	118	122	136	145
PR_3-Rh-Cen	133.0	132.8	133.8	133.6
PR_3-Rh-Br	94.4	87.4	89.5	91.1
PR_3-Rh-Ph	88.0	88.3	85.1	90.1
Cen-Rh-Ph	123.1	122.3	123.9	119.9
Cen-Rh-Br	120.9	121.9	119.0	118.5
Br-Rh-Ph	86.3	92.8	94.6	93.9
d(Rh-P)	2.248	2.274	2.290	2.306
d(Rh-Ph)	2.054	2.075	2.068	2.075

Future intramolecular studies will center on synthesizing the dihydrides of the formula $(C_5Me_5)Rh(PMe_2R)H_2$ where R = ethyl, butyl, pentyl, phenethyl, etc. and determining the kinetic and thermodynamic selectivity of each complex in neat alkane or arene solvent. In this fashion, we intend to determine the relative effect of chain length upon the selectivity of reaction. Temperature dependent behavior will permit the determination of the individual activation parameters $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ where necessary as was previously done with R=benzyl.

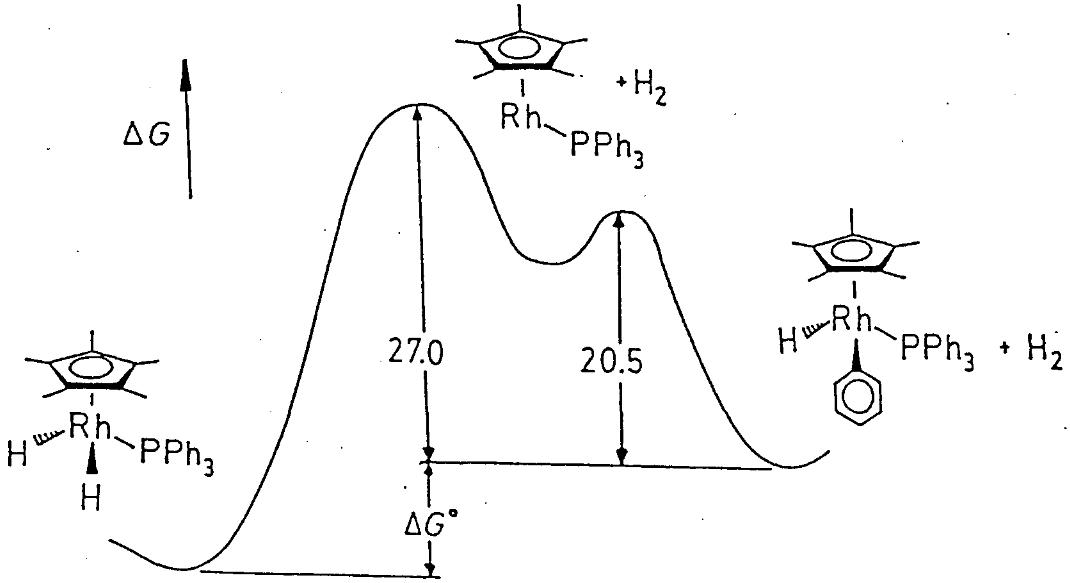
Studies of a related series of compounds beginning with $(C_5Me_5)Rh(PPh_3)H_2$ have also been initiated. In benzene solvent, $(C_5Me_5)Rh(PPh_3)(Ph)H$ is produced upon photolysis. This latter species was found to be labile at room temperature, and is observed to exchange in a few minutes with C_6D_6. Furthermore, the phenyl hydride complex reacts slowly with hydrogen to regenerate the dihydride.[7] If we can measure the thermal barrier to reductive elimination of hydrogen in this species, then we can establish the relative bond strengths of the Rh-Ph and Rh-H bonds as indicated in Scheme III.

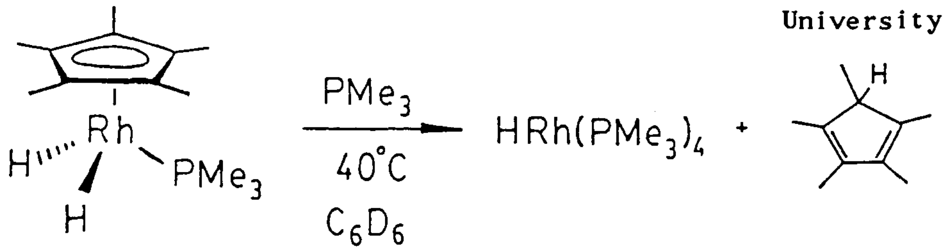
Attempts to heat $(C_5Me_5)Rh(PPh_3)H_2$ under D_2 does give $(C_5Me_5)Rh(PPh_3)D_2$ at about the same rate that $(C_5Me_5)Rh(PPh_3)(Ph)H$ reacts with H_2 (1 atm), but examination of the gas produced in the exchange reaction shows significant HD but little H_2 (Eq 6), indicating that the pathway for H/D exchange in $(C_5Me_5)Rh(PPh_3)H_2$ does <u>not</u> lie along the reaction coordinate shown in Scheme IV.[7] Bergman has found a very small difference between the Ir-Ph and Ir-H bonds,[8] and determination of these values for rhodium may help us to understand the higher selectivity displayed by rhodium in C-H bond activation reactions.



[6]

<u>Scheme IV.</u> Free Energy Diagram for $[(C_5Me_5)Rh(PPh_3)] + H_2$ in Benzene Solvent.



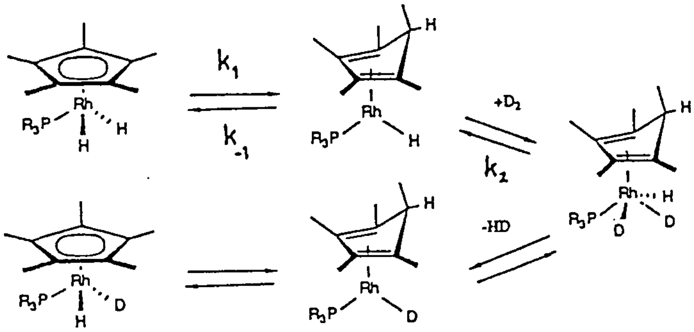


[7]

Furthermore, reaction of the dihydride complex with PMe_3 is found to cleanly produce pentamethylcyclopentadiene (C_5Me_5H) and $HRh(PMe_4)_4$ (Eq 7). These results together suggest that a hydride ligand may be migrating to the Cp^* ring to give a 16 electron Rh(I) intermediate that undergoes oxidative addition with the free D_2 gas (or ring displacement by PMe_3) as shown in Scheme V below. Further mechanistic studies of this reaction and its potential importance in C-H bond activation mechanisms will be described later.

Other studies underway with this compound will involve trapping of the incipient intermediate [(C_5Me_5)Rh(PPh_3)] with other in order to determine the thermal barrier for H_2 reductive elimination. If the PPh_3 complex undergoes decomposition prior to elimination of H_2, we will examine the related PPh_2Me and PMe_2Ph complexes were greater stability has been demonstrated.

Scheme V:



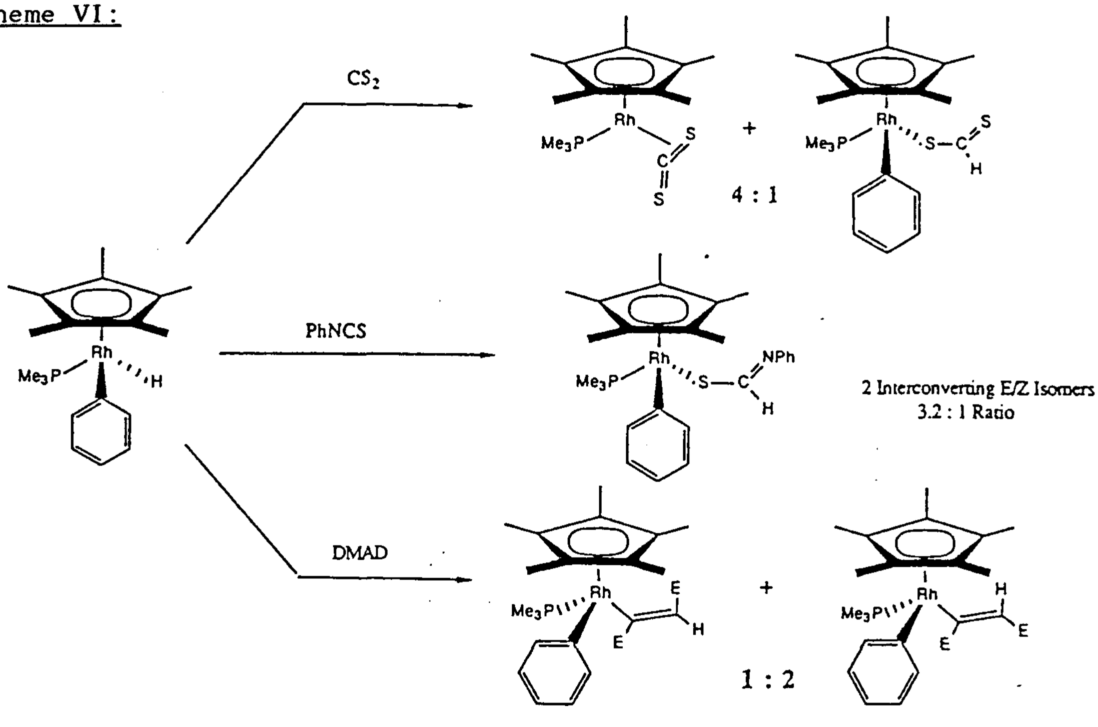
$$\text{Rate} = k_{obs}[\text{Rh}] = \frac{k_1 k_2 [D_2][\text{Rh}]}{k_2[D_2] + k_{-1}} \approx \frac{k_1 k_2 [D_2][\text{Rh}]}{k_{-1}}$$

$$\frac{k_1 k_2}{k_{-1}} \approx 5 \times 10^{-3}\, M^{-1} s^{-1}$$

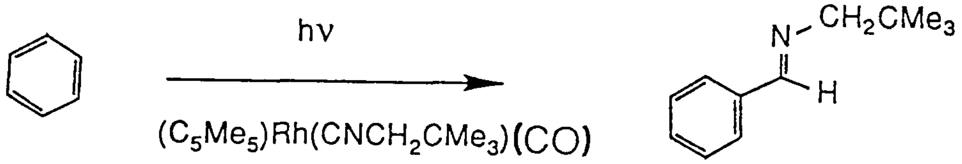
A.3. C-H Bond Functionalization.

The other area that we are actively pursuing involves the functionalization of species with have activated a C-H bond. In the previous grant period, we have shown that aryl and alkyl hydride rhodium complexes react with electron deficient acetylenes, CS_2, and PhNCS to produce complexes in which the substrate has inserted into the metal-hydrogen bond. These complexes have proven to be less than desirable for the efficient functionalization of C-H bonds. Scheme VI shows some reactions of small molecules with the $(C_5Me_5)Rh(PMe_3)(Ph)H$ complex. As can be seen, many result in either reaction with the Rh-H bond or reductive elimination of benzene. Of these, only the reaction with dimethylacetylenedicarboxylate gives organic products (substituted styrenes) upon oxidation with HI or iodine.[9]

Scheme VI:

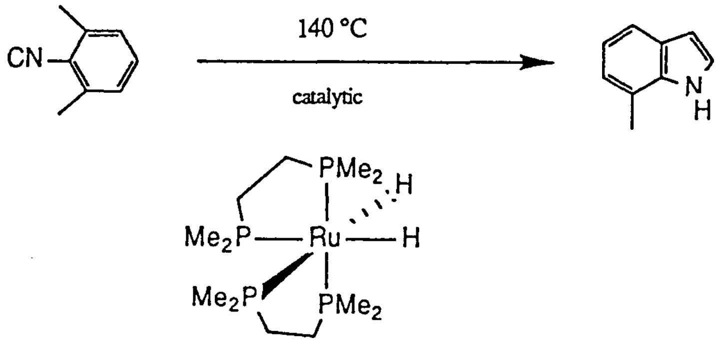


Another area that we are actively investigating involves the isocyanide complexes of the type $(C_5Me_5)Rh(CNR)_2$, and $(C_5Me_5)Rh(CNR)(CO)$.[10] Several of these species have been found to activate arene C-H bonds and effect their functionalization with isocyanide to produce aldimine products. Our initial work with $(C_5Me_5)Rh(CNR)_2$ where R = neopentyl demonstrated that UV photolysis (λ > 200 nm) in benzene gave the aldimine $C_6H_5CH{=}NR$ in ~30% yield. Labelling studies employing C_6D_6 indicated that the reaction probably did not proceed through the anticipated intermediate $[(C_5Me_5)Rh(CNR)]$, but rather through the species $[HRh(CNR)_3]$ following loss of the pentamethylcyclopentadiene ring to form tetramethylfulvene.[11] The addition of CO was found to promote this reaction by forming the substituted complex $(C_5Me_5)Rh(CNR)(CO)$, which gives higher yields of aldimine and uses a lower energy light source (λ > 300 nm, Eq 8).[12]



[8]

With regard to isocyanide functionalization, we have found other metals that serve much better for this purpose. The ruthenium complex $Ru(dmpe)_2(naphthyl)H$ was the first molecule reported to undergo reversible arene C-H bond activation at 60°C, and we have found this molecule reacts with o-methylphenyl isonitriles to generate indoles (Eq 9). The proposed mechanism involves initial formation of an isonitrile complex followed by dissociation of one end of a dmpe ligand. Metallation of the ortho methyl group C-H bond followed by isonitrile insertion and tautomerism gives the indole product. While this reaction is stoichiometric as written, reductive elimination permits the catalytic synthesis of indoles.[13] Extentions of these

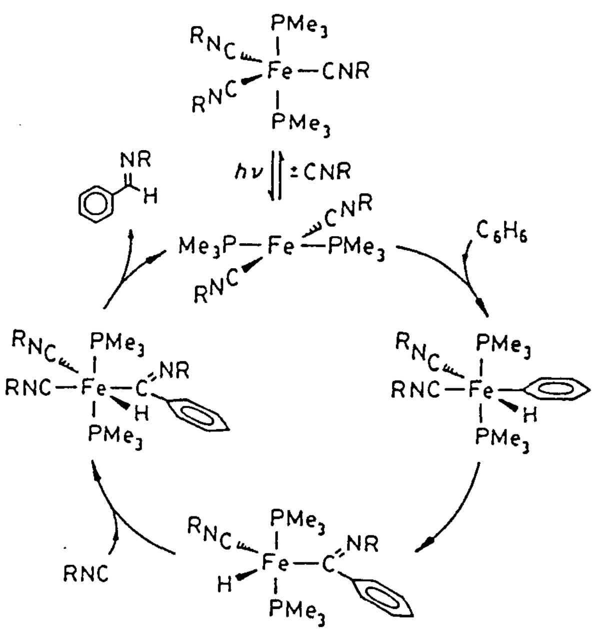


[9]

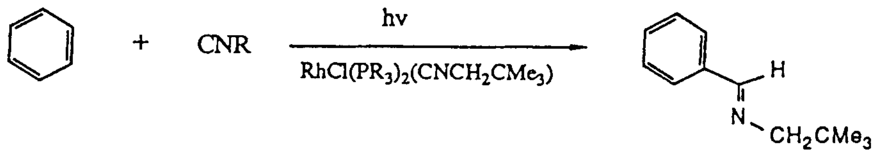
studies are leading in a separate direction from those proposed in this work, and we have obtained separate PRF funding for this work on heterocycle synthesis.

A series of new complexes $Fe(PMe_3)_2(CNR)_3$ have been prepared and found to be useful for catalytic arene functionalization. If the complex with R = neopentyl is irradiated with 313 nm light, the aldimine $(C_6H_5)CH{=}NCH_2CMe_3$ is produced in quantitative yield based on Fe. The metal fragment appears as an extremely air-sensitive disproportionation product $Fe(PMe_3)_3(CNR)_2$. We have evidence that irradiation of $Fe(PMe_3)_2(CNR)_3$ results in labilization of an isocyanide ligand (as opposed to thermal labilization of a phosphine ligand) and that the intermediate $[Fe(PMe_3)_2(CNR)_2]$ is responsible for oxidative addition to benzene. Subsequent isocyanide insertion and reductive elimination produces the aldimine product (Scheme VII). Irradiation of the complex in the presence of added isonitrile results in the catalytic production of aldimine from benzene and isonitrile. No alkane functionalization occurs upon irradiation in pentane, indicating that alkane C-H oxidative addition is probably not occurring with this first row transition metal.[14]

Scheme VII:



We have also prepared a series of complexes of the type $RhCl(PR_3)_2(CNR')$ where R = Me, Et, i-Pr and R'= neopentyl or 2,6-xylyl. Like the iron complexes, irradiation of the rhodium complexes in benzene solution containing low concentrations of added isonitrile results in the catalytic formation of aldimine products (Eq 10). Table IV shows the efficiency of the catalyst as a function of phosphine ligand and added isonitrile concentration.[15]



[10]

Table IV. Yield of aldimine using $RhCl(PR_3)_2(CNCH_2CMe_3)$ catalysts.

R	[Rh]	[CNR]	% Conversion	# Turnovers
i-Pr	0.20 mM	1.00 mM	76	4.5
	0.15	0.75	70	4.7
	0.10	0.50	72	4.3
	0.05	1.00	27	5.9
	0.05	0.50	68	7.7
Et	0.20	1.00	33	2.0
	0.15	1.00	30	2.3
	0.10	1.00	31	3.4
	0.05	1.00	10	2.0
Me	0.20	1.00	62	3.7

A.4. New Complexes that Activate C-H Bonds.

The initial budget period of this grant has also enabled us to initiate studies of a series of rhenium phosphine polyhydrides. We have prepared and characterized structurally a series of trihydrides in this group, including $ReH_3(dmpe)_2$, $MnH_3(dmpe)_2$, and $ReH_3(PMe_3)_4$. Some of these species have shown the ability to catalytically activate alkane C-H bonds for H/D exchange.

The manganese complex $MnH_3(dmpe)_2$ has been studied in some detail.[16] On the basis of temperature dependent T_1 measurements, the trihydride complex is more appropriately formulated as an η^2-dihydrogen monohydride complex. The E° for oxidation of the complex (reversible $1e^-$ couple at -0.85 V vs NHE by CV) falls in between that measured for $MnH(CO)(dmpe)_2$ (-0.30 V) and $MnH(C_2H_4)(dmpe)_2$ (-1.02 V), also suggesting a Mn(I) formulation. By comparison, $[FeH_3(dmpe)_2]^+$ and $[FeH_3(dppe)_2]^+$ have both been formulated as η^2-dihydrogen complexes.[17] The complex readily loses H_2, and in C_6D_6 solution H/D exchange is seen with the hydride ligands (Eq 11). Slow exchange of the dmpe methyl and methylene hydrogens is also observed. Again, no H/D exchange is seen with perdeuteroalkanes with this first row metal, despite the observations made by Field with $FeH_2(dmpe)_2$.

$$MnH_3(dmpe)_2 \xrightarrow[C_6D_6]{30°C} MnD_3(dmpe)_2 \xrightarrow{slow} MnD_3(dmpe\text{-}d_{16})_2 \qquad [11]$$

The rhenium complex $ReH_3(PMe_3)_4$ shows similar behavior, although higher temperatures are required to labilize H_2. Thermal exchange of the hydride and phosphine hydrogens with those of C_6D_6 solvent occurs upon heating to 90°C (Eq 12). Under similar conditions in perdeuteroalkane solvent, no H/D exchange is seen.

$$ReH_3(PMe_3)_4 \xrightarrow[C_6D_6]{90°C} ReD_3(PMe_3)_4 \xrightarrow{slow} ReD_3[P(CD_3)_3]_4 \qquad [12]$$

The rhenium analog $ReH_3(dmpe)_2$, however, is found to behave somewhat differently. H/D exchange of the hydride ligands with C_6D_6 can be effected either thermally (160°C) or photochemically. However, no exchange of the dmpe hydrogens is observed, even after prolonged irradiation. Furthermore, the complex now catalyzes H/D exchange between a 1:1 mixture of hexane and C_6D_6 and between a mixture of THF and C_6D_6 (Eq 13). $ReH_3(depe)_2$ exchanges hydrides with aromatic hydrogens, but does not activate alkanes or exchange hydrogens in the ligand ethyl groups.

$$ReH_3(dmpe)_2 \xrightarrow[\text{hexane}/C_6D_6]{h\nu} CD_3CH_2CH_2CH_2CH_2CD_3 \qquad [13]$$

No details are known about the exchange mechanisms. It is clear that the relative changes in metal size and ligand steric effects strongly influence the types of C-H bonds that the metal can activate. X-ray structural studies of these complexes are in progress that will help provide data for comparison with the results of the selectivity studies.

B. Summary

The functionalization reactions of $(C_5Me_5)Rh(PMe_3)(R)H$ have been limited to reactions with electrophiles, usually resulting in insertion into the Rh-H bond with no further elimination. The thermodynamic and kinetic studies of the complexes $(C_5Me_5)Rh(PR_3)(Ph)H$ have shown that intramolecular cyclometallation of the P-phenyl group is disfavored both kinetically and thermodynamically with respect to intermolecular activation of arene solvent. Successful aromatic C-H bond functionalization has been achieved by employing isonitriles as the trapping reagent. CO has been found to promote this insertion in the $(C_5Me_5)RhL$ system, whereas the reaction is catalytic at low [CNR] with an iron(0) phosphine complex. $[Ru(dmpe)_2]$ has been shown to be an effective catalyst for the formation of heterocyclic indoles, and is proceeding towards development. Finally, new rhenium complexes have been prepared and discovered to catalyze H/D exchange reactions with a variety of hydrocarbons. Extension of the chemistry of these species to include isonitrile functionalization is under investigation.

This research has proceeded in very good accord with our renewal research proposal. We take our observations as support of our general notions about the ability of transition metal complexes to effect the activation of C-H bonds of alkanes and arenes. The observation of η^2-arene complexes provides further support for our proposal that they are important in C-H activation, and will be the focus of future studies.

C. References and Notes

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D. Publications

The work under DOE support has been published in the following articles:

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"The Preparation, Characterization, and Catalytic Functionalization of C-H Bonds by $RhCl(PR_3)_2(CNR')$," William D. Jones and Edward P. Hessell, in preparation.