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Photochemical C−H Activation and Ligand Exchange Reactions of $CpRe(PPh_3)_2H_2$. Phosphine Dissociation Is Not Involved

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The dihydride $CpRe(PPh_3)_2H_2$ (**1**) catalyzes H/D exchange between C_6D_6 and other arenes or alkanes. Compound **1** also undergoes photochemical phosphine substitution with PMe_3 to give $CpRe(PPh_3)(PMe_3)H_2$ and then $CpRe(PMe_3)_2H_2$. Mechanistic studies of these reactions are inconsistent with $[CpRe(PPh_3)H_2]$ as an intermediate. An alternative mechanism is presented proposing that the active species for H/D exchange is the 14-electron cyclic allyl intermediate $[(\eta^3\text{-}C_5H_7)Re(PPh_3)_2]$ (**E**), in which both hydrides have migrated from the rhenium to the cyclopentadienyl ligand. This intermediate accounts for the fact that (1) deuterium does not exchange into the hydride ligands of complex **1** during the H/D exchange catalysis and (2) phosphine substitution occurs by an associative pathway. The precursor to intermediate **E**, $[(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H]$ (**D**), can undergo reversible orthometalation, allowing H/D exchange between the hydride ligands and the ortho phosphine positions. Evidence is presented to support this new mechanism as well as to rule out other feasible mechanisms.

Introduction

The intermolecular activation and functionalization of C−H bonds in arenes and (more importantly) alkanes has been an area of extensive research for almost three decades now, since the discovery of cyclometalation in the early 1960s.[1] Since then, there have been many examples of transition-metal complexes capable of activating C−H bonds,[2] and there have been several studies that ascertain the relative thermodynamic stabilities and strengths of various metal−carbon bonds for a given R−M−H series.[3] Two common pathways identified for C−H activation that are important to organometallic chemists are electrophilic metathesis and oxidative addition.[4]

In general, the complexes that have been shown to be capable of oxidatively adding C−H bonds contain electron-rich metal centers in low oxidation states. The ligands used in these systems are typically Cp (or Cp*), phosphines, and/or hydrides. One such complex that was found to be able to activate C−H bonds photochemically was $CpRe(PPh_3)_2H_2$ (**1**).[5] Earlier studies showed that **1** was capable of catalyzing H/D exchange between a deuterated solvent (typically benzene or THF) and a variety of arene and alkane substrates, including methane (eq 1). Turnover numbers exceeded 1000 for THF

$$\mathrm{C_6D_6} + \mathrm{RH} \xrightarrow[h\nu]{\mathrm{CpRe(PPh_3)H_2}} \mathrm{C_6D_5H} + \mathrm{RD} \tag{1}$$

$$\mathrm{RH} = \mathrm{C_6H_6,\ CH_4,\ C_2H_6,\ C_3H_8},\ c\text{-}\mathrm{C_3H_6},\ c\text{-}\mathrm{C_5H_{10}},\ \mathrm{THF,\ Et_2O}$$

or diethyl ether in C_6D_6. The mechanism originally proposed for the catalytic H/D exchange is typical of that invoked for other H/D exchange systems, namely, the photochemical loss of PPh_3 to generate the 16-electron fragment $[CpRe(PPh_3)H_2]$, which was then active in H/D exchange (Scheme 1).

There were several experiments conducted that helped support this mechanism. The H/D exchange was completely inhibited upon addition of small amounts of triphenylphosphine. Also, irradiation of **1** in the presence of phosphines, CO, and CNR leads to the formation of substituted products of the type $CpRe(PPh_3)(L)H_2$ and $CpRe(L)_2H_2$.[6] One observation which did *not* support the proposed mechanism was that the ^{1}H NMR resonance for the hydride ligands of **1** at δ −9.95 (t, J = 40.1 Hz, 2 H) always integrated as two protons, even after the hundreds or thousands of turnovers of H/D exchange. This observation is difficult to reconcile with the mechanism proposed in Scheme 1, as all known polyhydrides which catalyze H/D exchange among hydrocarbons via oxidative addition/reduction elimination incorporate

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[1] (a) Kliman, J. P.; Dubeck, M. *J. Am. Chem. Soc.* **1963**, *85*, 1544−1545. (b) Horiie, S.; Murahashi, S. *Nippon Kagaku Zasshi* **1960**, *33*, 247−251. (c) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403−424.

[2] (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245−269. (b) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Boston, 1984.

[3] (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929−3939. (b) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537−1550. (c) Wax, M. J.; Stryker, J. M.; Buchanan, M.; Kovac, C. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 1121−1122. (d) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650−1663. (e) Nolan, S. P.; Hoff, C. D.; Stoutland, P. O.; Newman, L. J.; Buchanan, J. M.; Bergman, R. G.; Yang, G. K.; Peters, K. S. *J. Am. Chem. Soc.* **1987**, *109*, 3143−3145. (f) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41−48. (g) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1993**, *115*, 554−562.

[4] Hill, C. L. *Activation and Functionalization of Alkanes*; Wiley: New York, 1989.

[5] Jones, W. D.; Maguire, J. A. *Organometallics* **1986**, *5*, 590−591.

[6] Jones, W. D.; Maguire, J. A.; Rosini, G. P. *Inorg. Chim. Acta* **1998**, *270*, 77−86.

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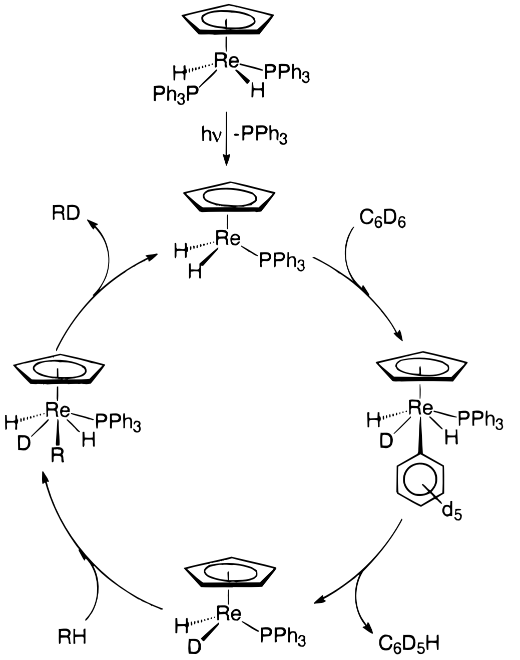
Scheme 1. "Simple" H/D Exchange Mechanism



deuterium into the hydride positions of the catalyst. The studies presented in this paper shed light on the photochemistry of **1**, in terms of both the phosphine substitution and the H/D exchange reaction. A new mechanism is proposed that builds upon literature precedents involving migration of the hydride ligands to the Cp ring.

Results

Preparation and H/D Exchange Reactivity of CpReH$_2$(PPh$_3$)$_2$ (1). The reaction of ReH$_7$(PPh$_3$)$_2$ with excess cyclopentadiene in THF yields the η^4-cyclopentadiene complex (η^4-C$_4$H$_6$)ReH$_3$(PPh$_3$)$_2$, which is easily converted to **1** by the thermal loss of H$_2$ at 60 °C.[7] Thermolysis of samples of **1** at elevated temperatures (up to 220 °C) results in no reaction (either ligand exchange with phosphine or solvent activation), as evidenced by NMR spectroscopy.[6] As mentioned above, however, photolysis of samples of **1** ($\lambda > 345$ nm) shows evidence for both ligand exchange reactions (with a variety of σ-donor ligands) and reversible C−H activation reactions (by H/D exchange with deuterated solvents). The UV−vis spectrum of **1** in C$_6$H$_6$ shows a well-defined absorption maximum at 328 nm ($\epsilon = 1413$ M^{-1} cm^{-1}; Figure 1). Table 1 shows several examples of the H/D exchange reactions catalyzed by **1**. Figure 2 shows how the H/D exchange is initially linear but slows with continued irradiation due to the formation of small amounts of PPh$_3$ that are produced by the slow photodecomposition of **1**. Free PPh$_3$ (~1−2%) is observed in these samples as the photolysis proceeds. The H/D exchange can be completely inhibited by the addition of free PPh$_3$ to the initial solution.

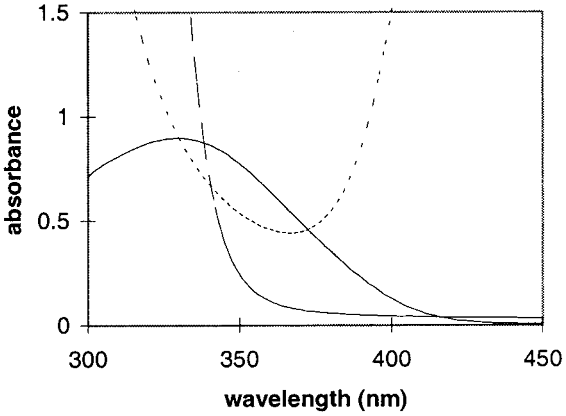


Figure 1. UV−vis spectrum of **1** in C$_6$H$_6$. The absorbances of the 365 nm band-pass and 345 nm long-pass filters used are also shown.

Table 1. Photochemical H/D Exchange Reactions Catalyzed by CpRe(PPh$_3$)$_2$H$_2$ in C$_6$D$_6$[a]

alkane	[alkane], M	irradiation time, min	no. of turnovers
methane	~0.04	180	68
ethane	2	300	33
propane	2	60	51,[c] 2.5[d]
		120	72,[c] 4.0[d]
		180	77,[c] 4.0[d]
cyclopropane	5	40	250
		70	369
		120	409
		180	423
cyclopentane	1.2	30	42
		70	74
		120	87
		300	90
THF[b]	6.2	60	488,[e] 840[f]
		100	520,[e] 895[f]

[a] [CpRe(PPh$_3$)$_2$H$_2$] = 1.2 mM. [b] [CpRe(PPh$_3$)$_2$H$_2$] = 0.6 mM. [c] Primary exchange. [d] Secondary exchange. [e] β exchange. [f] α exchange.

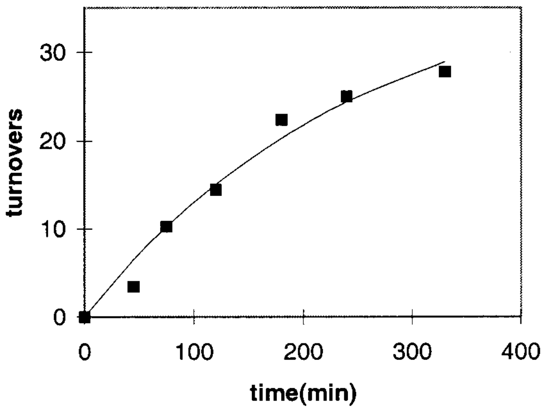


Figure 2. Photocatalyzed H/D exchange between *n*-pentane and C$_6$D$_6$ by **1**.

As indicated in Table 1, the primary C−H bonds of propane are much more reactive than the secondary C−H bonds, yet the secondary bonds of cyclopentane are as reactive as the primary C−H bonds of propane in independent experiments. Figure 3 shows a plot of the H/D exchange between propane and C$_6$D$_6$ solvent as a function of alkane concentration. From the initial rates of exchange, the reaction appears to be first order in propane concentration.

In addition, competition studies were performed using a mixture of alkanes in C$_6$D$_6$. Irradiation of **1** in the presence of a CH$_4$/C$_2$H$_6$ mixture (100 equiv each) revealed a 2:1 kinetic selectivity for H/D exchange into methane vs ethane on a per-molecule basis. Similarly,

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(7) Jones, W. D.; Maguire, J. A. *Organometallics* **1987**, *6*, 1301−1311.

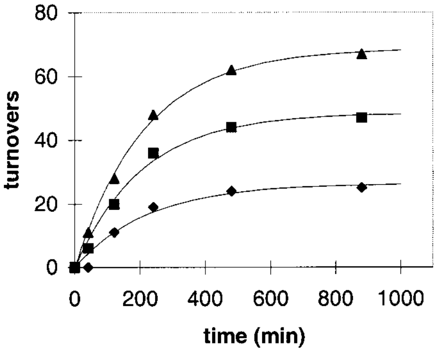


Figure 3. Effect of propane concentration on H/D exchange with benzene-d_6 catalyzed by **1**: (▲) 3.84 M; (■) 2.56 M; (◆) 1.28 M.

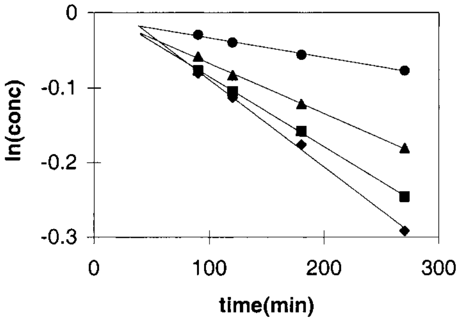


Figure 4. Effect of [PMe$_3$] on phosphine photosubstitution rate: (●) 0.0053 M; (▲) 0.027 M; (■) 0.109 M; (◆) 0.574 M.

Table 2. Effect of [PMe$_3$] on Rates of Phosphine Photosubstitution in 1

sample	[PMe$_3$], M	k_{obsd}, s^{-1}
1	0.0053	$[4.3(9)] \times 10^{-6}$
2	0.027	$[1.12(13)] \times 10^{-5}$
3	0.109	$[1.56(11)] \times 10^{-5}$
4	0.574	$[1.95(31)] \times 10^{-5}$

a competition between CH_4 and c-C_5H_{10} (100 equiv each) revealed a 1.6:1 preference for methane exchange over the secondary C−H bonds of cyclopentane. A competition between benzene and propane (100 equiv each) in THF-d_8 solvent as deuterium source produced an 8.2:1 preference for benzene exchange over propane primary C−H exchange.

Phosphine Exchange Study. Four samples of **1** in C_6D_6 (5.1×10^{-3} M) were prepared containing different excess amounts of PMe$_3$, as shown in Table 2. The samples were then irradiated (λ >345 nm) using a merry-go-round apparatus. The phosphine exchange was followed by ^{1}H NMR spectroscopy by monitoring the ratio of the ortho phosphine protons of **1** with those of the monosubstituted product CpRe(PPh$_3$)(PMe$_3$)H$_2$. Short irradiation times were used to avoid the formation of the disubstituted CpRe(PMe$_3$)$_2$H$_2$. Plots of ln([**1**]/[**1**]$_0$) vs time are linear, with the slope varying with the concentration of PMe$_3$ (Figure 4, Table 2).[8]

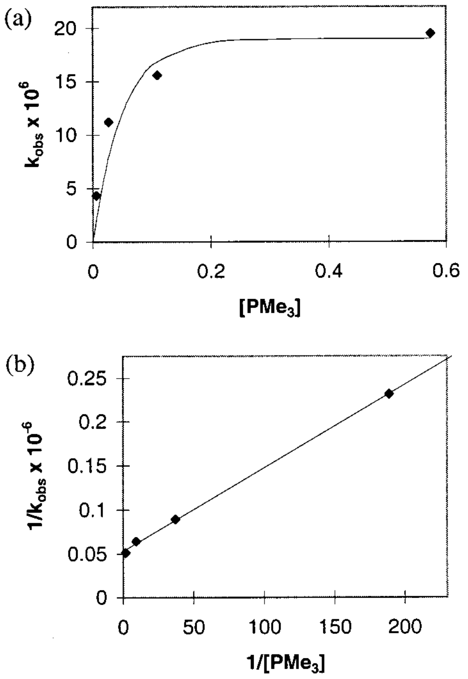
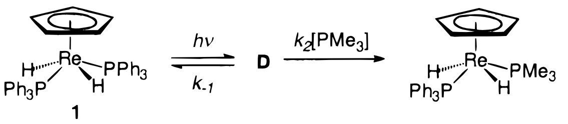


Figure 5. Dependence of k_{obsd} on [PMe$_3$] for the photosubstitution of **1**: (a) k_{obsd} vs [PMe$_3$]; (b) $1/k_{\mathrm{obsd}}$ vs 1/[PMe$_3$].

A kinetic scheme for the photochemical associative exchange of PPh$_3$ in **1** with PMe$_3$ is shown in eq 2. If



(2)

one assumes steady-state conditions on the intermediate **D**, then one can solve the kinetic expression for the disappearance of **1** and for k_{obs} as shown in eqs 3 and 4.

rate = (rate of formation of **D**) ×
(fraction of **D** that goes on to form **2**)

$$-\frac{d[\mathbf{1}]}{dt} = I_0\frac{[\mathbf{1}]}{[\mathbf{1}]_0}A\Phi_A\frac{k_2[\mathrm{PMe}_3]}{k_{-1} + k_2[\mathrm{PMe}_3]} = k_{\mathrm{obsd}}\frac{[\mathbf{1}]}{[\mathbf{1}]_0} \quad (3)$$

$$k_{\mathrm{obsd}} = \frac{k_1 k_2[\mathrm{PMe}_3]}{k_{-1} + k_2[\mathrm{PMe}_3]} \quad (4)$$

In this analysis, I_0 is the incident light intensity, [**1**]/[**1**]$_0$ is the fraction of light absorbed by **1**, A is the area of the sample being irradiated, and Φ_A is the quantum yield for formation of **D**. Since all of these quantities except [**1**]/[**1**]$_0$ are constant for the series of irradiations, they are lumped together as the rate constant k_1 in eq 4.

This scheme predicts that k_{obsd} should be dependent on the concentration of PMe$_3$ used and that the reaction should follow saturation kinetics. Figure 5a shows that this is indeed the case. Note that a direct associative attack by PMe$_3$ on the excited state of **1** would not be expected to show saturation behavior. From eq 4, a plot of $1/k_{\mathrm{obsd}}$ versus 1/[PMe$_3$] should be linear with a slope of k_{-1}/k_1k_2 and an intercept of $1/k_1$. Figure 5b shows this plot, the intercept and slope of which give $k_1 = [1.9(3)] \times 10^{-5}$ s^{-1} and $k_{-1}/k_2 = [1.8(2)] \times 10^{-2}$ M. These data

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(8) The solutions used in these studies were optically dense in the near-UV region,and the incident photon flux is constant. Consequently, one might expect a plot of the disappearance of **1** vs time to be linear rather than logarithmic, as seen in the first few turnovers of H/D exchange. The product CpRe(PPh$_3$)(PMe$_3$)H$_2$ has a UV spectrum very similar to that of **1**, however, and consequently the inner filter effect gives rise to an exponential decay of **1**. That is, as the reaction proceeds a smaller fraction of the light is being absorbed by **1**, and hence its rate of decay slows.

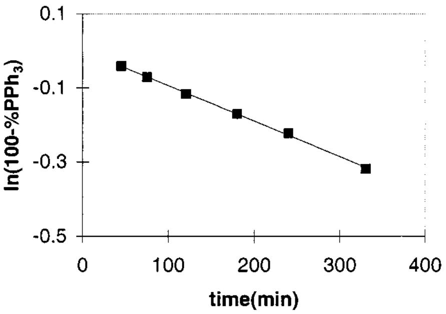


Figure 6. Photochemical exchange of PPh$_3$-d_{15} into **1**.

support an associative mechanism for phosphine exchange with the photochemically formed intermediate **D**. An alternative explanation for saturation behavior, namely that the rate is being limited by the photon flux (i.e., $\Phi_{\text{substitution}} \approx 1$), is unlikely in that this would require that the excited state be sufficiently long-lived to undergo bimolecular reaction with PMe$_3$. This possibility can also be discounted, as these substitution reactions (qualitatively) have quantum yields that are substantially less than 1.

Comparison of the Rates of H/D Exchange and Phosphine Exchange. Since both ligand exchange and H/D exchange occur via associative mechanisms, the relative rates of these two reactions can be compared if the substrate concentrations are known. Two NMR samples of **1** in C$_6$D$_6$ (5.14×10^{-3} M) were prepared. To the first sample was added excess PPh$_3$-d_{15} (0.224 M), and to the second sample was added excess *n*-pentane (0.88 M).[9] The two samples were irradiated through a 345 nm filter, and a merry-go-round apparatus was used to ensure that both samples received the same number of photons. The phosphine exchange reaction was monitored by integrating the ortho resonances of bound and free PPh$_3$-d_0 (by ^{1}H NMR spectroscopy). The appearance of free PPh$_3$-d_0 is exponential (Figure 6), and fitting to eq 5 gives $k_{\text{obsd}} = [1.60(8)] \times$

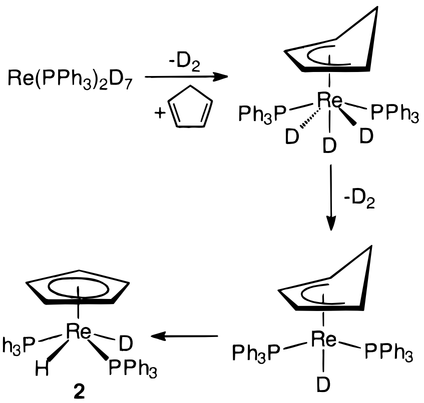
$$[\mathrm{PPh_3}\text{-}d_0] = 2[\mathbf{1}]_0(1 - \mathrm{e}^{-k_{\text{obs}}t}) \qquad (5)$$

10^{-5} s^{-1}. The H/D exchange catalysis was followed by monitoring the ratio of the internal standard c-C$_6$D$_{12}$ to *n*-pentane-*d* by ^{2}H NMR. The number of turnovers was then calculated as shown in eq 6. A plot of turnover

$$\text{no. of turnovers} = 12\left(\frac{\text{area}(\mathrm{C_5H_{11}D})}{\text{area}(\text{c-}\mathrm{C_6D_{12}})}\right)\left(\frac{\text{mol of c-}\mathrm{C_6D_{12}}}{\text{mol of Re}}\right) \qquad (6)$$

number vs time is linear for ~3 h (25 turnovers), after which time the catalyst decomposition begins to inhibit the reaction. From the slope of this line, $k_{\text{obsd}} = [2.1(4)] \times 10^{-3}$ s^{-1} for H/D exchange. After correcting the observed first-order rates of H/D exchange and phosphine exchange for the substrate concentrations, we found that *n*-pentane-*d* is formed at a rate of ~37 times faster than the rate at which phosphine exchange takes place.

Scheme 2



Reaction of CpReH$_2$(PPh$_3$)$_2$ with D$_2$. To test for the photodissociation of H$_2$ from **1**, a sample of **1** in C$_6$D$_6$ (5.14×10^{-3} M) was placed under an atmosphere of D$_2$ and the sample irradiated through a 345 nm filter. If H$_2$ dissociation were occurring, then one would expect to see the rapid formation of CpReD$_2$(PPh$_3$)$_2$ and free H$_2$. The reaction was followed by ^{1}H NMR spectroscopy, which showed the slow formation of CpReD$_n$H$_{4-n}$(PPh$_3$), where integration indicates $n = 2$. The hydride resonance of **1** remains sharp throughout the reaction and does not show a decrease in intensity relative to the phosphine or Cp resonances which would be expected for the direct formation of CpReD$_2$(PPh$_3$)$_2$. It therefore seems reasonable that **1** does not lose H$_2$ upon photolysis.

Preparation and Reactivity of CpReHD(PPh$_3$)$_2$ (2). The reaction of ReD$_7$(PPh$_3$)$_2$ with excess CpH at 60 °C results in the formation of CpReHD(PPh$_3$)$_2$, as shown in Scheme 2.[7] The ^{1}H NMR spectrum of **2** is essentially identical with that of **1**, except that the hydride resonance integrates as one hydride instead of two. The hydride-coupled ^{31}P NMR spectrum of **2** shows a broad doublet, also indicating the presence of only one metal hydride. The photochemistry of **2** was examined to see if both the hydride and the deuteride ligands would be preserved during catalytic H/D exchange, analogous to what was seen for **1**.

A sample of **2** in C$_6$D$_6$ (5.14×10^{-3} M) was prepared with *n*-pentane (0.05 mL, 10% v/v) added as the substrate, and the sample was then irradiated through a 345 nm filter. Surprisingly, in addition to H/D exchange catalysis as observed for **1**, the deuteride ligand of **2** was observed to diminish with time (over 100 h), as evidenced by an increase in the M–H resonance in the ^{1}H NMR spectrum. A similar experiment in C$_6$H$_6$ solvent showed the loss of the Re–D resonance by ^{2}H NMR spectroscopy. Similar observations of the loss of deuteride ligand in **2** were seen upon irradiation in neat C$_6$D$_6$, methylcyclohexane-d_{14}, *n*-pentane, or THF. As mentioned earlier, irradiation of **1** in C$_6$D$_6$ or methylcyclohexane-d_{14} under identical conditions did not result in the formation of **2**, nor was **2** formed during any of the catalytic H/D exchange reactions.

The observed incorporation of hydrogen into the deuteride resonance of **2** during photolysis is in apparent contrast with the observation that **1** never exhibits deuterium exchange into its hydride resonance during H/D exchange between solvents. These two observations can be accommodated, however, if the pathway that is

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[9] Trimethylphosphine was not used for this study in order to eliminate any effects that changes in the UV–vis spectra of the substituted complexes (A and/or ϵ) might introduce into the kinetics of the reaction mechanism due to changes in the amount of light absorbed during the reaction. See: Drolet, D. P.; Lees, A. J. *J. Am. Chem. Soc.* **1992**, *114*, 4186–4194.

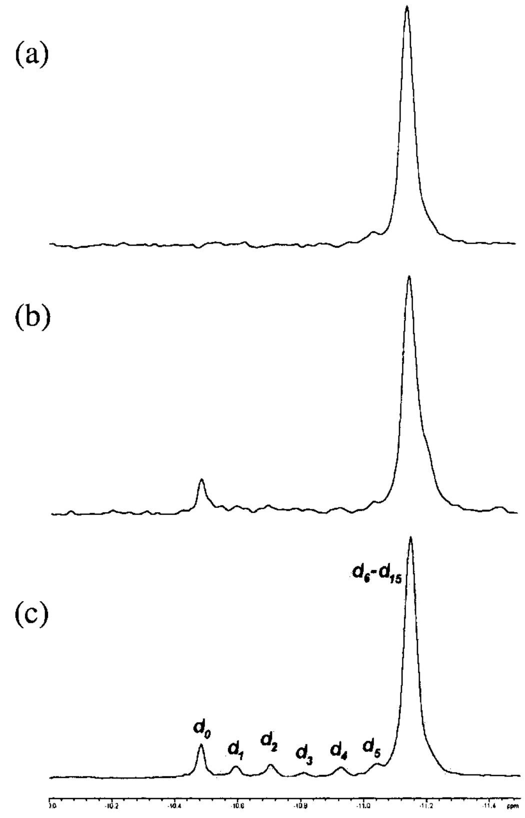
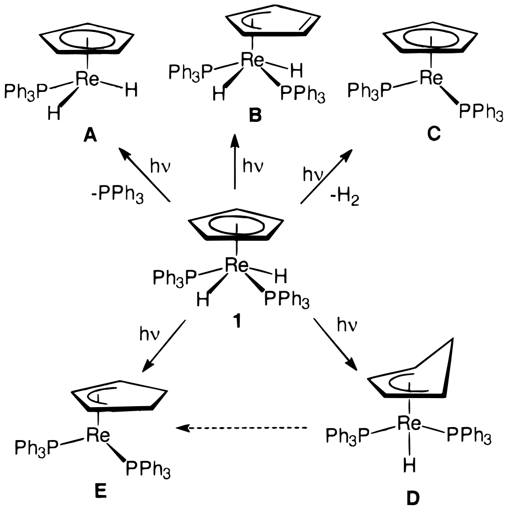


Figure 7. H/D exchange into the ortho-phenyl phosphine positions of PPh_3: (a) initial $^{31}P\{^1H\}$ spectrum of **1** + PPh_3-d_{15} (5 equiv) in C_6D_6 (region shown is for free PPh_3 in solution); (b) $^{31}P\{^1H\}$ spectrum after 28 h irradiation, showing the formation of PPh_3-d_0; (c) $^{31}P\{^1H\}$ spectrum after 99 h irradiation, showing the formation of PPh_3 with 0−6 ortho-phenyl deuterium atoms.

responsible for the observed H/D exchange catalysis is *not* the pathway that is responsible for the loss of deuteride in **2**, but rather, there is a second competing pathway that is acting to remove the deuterium from the metal center in **2**. One pathway that could explain the removal of deuterium from the metal center in **2** is the cyclometalation of one of the PPh_3 ligands. This reaction could then result in the monodeuteration of the PPh_3 upon reductive elimination and the apparent formation of **1**, since the hydride resonance now integrates as two protons and little change would be observed in the PPh_3 multiplet resonance of **1**. Evidence for orthometalation has in fact been obtained in the experiments described below.

Irradiation of **1** in C_6D_6 in the presence of a 6-fold excess of PPh_3-d_{15} initially results in the formation of free PPh_3-d_0 by ligand exchange with **1**. The hydride resonance is unchanged, integrating as two protons. With continued irradiation, the hydride resonance is seen to diminish relative to the Cp resonance for **1**. In addition, the free triphenylphosphine-d_0 is observed to slowly incorporate deuterium into the ortho positions of the phenyl groups, as some of the triphenylphosphine-d_{15} is seen to incorporate hydrogen. This exchange can be easily monitored by ^{31}P NMR spectroscopy, where there is a monotonic upfield intrinsic isotope shift of ~0.1 ppm per ortho phenyl deuterium exchanged into free PPh_3 (Figure 7). The distribution of species is consistent with a stepwise exchange of ortho-H for ortho-D and vice versa. A slight preference is observed for the incorporation of two deuterium atoms at a time. Examination of the resonance for **1** at δ 30.81 shows its replacement by a downfield singlet at δ 30.24 for $CpReH_2(PPh_3)_n$-$(P(C_6D_5)_3)_{2-n}$. These multiple H/D exchanges can only occur if both phosphine substitution and H/D exchange between the hydride ligands and the ortho hydrogens are occurring, with the former proceeding more rapidly. Examination of the free PPh_3 by mass spectroscopy after 250 h of irradiation confirms the presence of d_0−d_{15} isotopomers.

Scheme 3



Discussion

Mechanism for Photochemical H/D Exchange of 1. Since the mechanism in Scheme 1 does not adequately explain the observed behavior of the hydride ligands of **1** during H/D exchange catalysis or the associative phosphine exchange, a new mechanism is necessary to explain the photochemistry of **1**. Scheme 3 summarizes several photochemical reaction pathways for **1**, all of which generate unsaturated intermediates that might lead to a catalytic cycle for H/D exchange. Of the five pathways shown, only those forming intermediates **C** and **E** are capable of explaining the lack of deuterium incorporation during H/D exchange, since they are the only pathways in which both hydrogen atoms are removed from the metal center during catalysis. The three remaining pathways should all show rapid deuterium incorporation, since there will be both a hydride and a deuteride at the metal center during catalysis. The originally proposed intermediate (**A**) is inconsistent with both the lack of deuterium incorporation into **1** and the associative phosphine substitution (with saturation behavior) into **1**.[5] Intermediate **B** involves formation of a 16-electron η^3-C_5H_5 intermediate (Cp slippage[10]) which also would be expected to exchange deuterium into the hydride positions. Additional evidence against intermediate **B** is the fact that the analogous indenyl complex (η^5-indenyl)Re-$(PPh_3)_2H_2$ undergoes *no* net photochemistry, either

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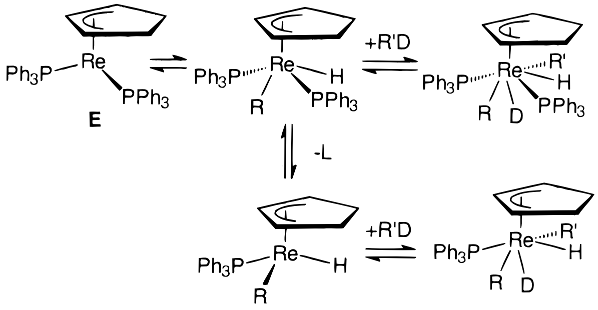
photosubstitution or H/D exchange catalysis, upon irradiation.[11] Intermediate **C** is ruled out, as **1** does not undergo exchange of hydride ligands for deuteride ligands upon irradiation under D_2.

As intermediates **A**−**C** are inconsistent with our observations, intermediates **D** and **E** were also considered. The first intermediate (**D**) arises by way of migration of a hydride ligand to the C_5H_5 ring. Reversible cyclometalation of this species would allow for H/D exchange between the hydride ligand and the ortho-phenyl of the PPh_3 ligand. This cyclometalated intermediate is similar to the known complex (η^4-C_4H_6)Re-$(PPh_3)_2H_3$, but with a cyclometalated phenyl ring replacing one of the hydride ligands.[7] Intermediate **D** is apparently not capable of activating C−H bonds intermolecularly; otherwise, H/D exchange of the hydride ligand would be expected to occur. Intermediate **D** could also account for the associative phosphine substitution observed in **1**. This 16-electron intermediate has a choice of either undergoing associative substitution by PMe_3 or undergoing migration of the endo C_5H_6 hydrogen back to the metal center. This type of branching from a photogenerated intermediate is precisely what the kinetic scheme in eqs 2−4 requires.

To account for the lack of exchange of the hydride ligands upon catalysis of H/D exchange between substrates, migration of *both* hydride ligands to the η^4-C_5H_6 group is postulated. This migration would generate the 14-electron π-allyl intermediate **E,** which is responsible for the observed H/D exchange catalysis of **1** by oxidative-addition/reductive-elimination pathways involving Re^{III} and Re^{V} intermediates. Two possible pathways for the formation of the allyl species are (1) a concerted double-hydride migration and (2) a single photochemical hydride migration to form **D**, which can then form the allyl species **E** by the rapid migration of the remaining hydride ligand. The rapid and reversible migration of a hydride ligand to an η^4-C_5H_6 ligand to generate an η^3-allyl ligand has been seen before in the closely related complex (η^4-C_5H_6)$ReH_3(PPh_3)_2$;[7] therefore, it is plausible that it could occur in **D** also. In addition, earlier H/D exchange catalysis using $Re(PPh_3)_2H_7$ indicated that the formation of a 14-electron rhenium complex was required for alkane activation.[12] Other 14 e^- complexes have also been invoked in alkane activation reactions.[13] Intermediate **D** can also be responsible for the formation of $CpRe(PPh_3)H_2D_2$ upon irradiation of **1** in the presence of D_2. (η^4-C_5H_6)$ReH_3(PPh_3)_2$ is known to generate CpRe-$(PPh_3)H_4$ upon photolysis.[7]

Two pathways by which intermediate **E** can catalyze H/D exchange between hydrocarbons are shown in Scheme 4. In one of these, **E** oxidatively adds first one substrate and then the other, with Re^{III} and Re^{V} intermediates involved. The second pathway is similar but shows that phosphine might be lost prior to the second oxidative addition. This variation allows for the inhibition of intermolecular H/D exchange by added phosphine. Alternatively, phosphine might interfere with H/D exchange by tying up the vacant site on one of the coordinatively unsaturated intermediates.

Scheme 4



Conclusions

In summary, it is apparent that **1** and **2** photochemically undergo a single metal to ring hydride migration but that the resulting 16-electron intermediate [(η^4-C_5H_6)$ReH(PPh_3)_2$] is not capable of catalyzing H/D exchange between a solvent and substrate. It can, however, reversibly cyclometalate one of the PPh_3 ligands present (which is responsible for the removal of deuterium from the metal center of **2**) or undergo a second (rapid and reversible) metal to ring hydride migration, as seen previously in the analogous (η^4-C_5H_6)$ReH_3(PPh_3)_2$, to form the 14-electron intermediate [(η^3-C_5H_7)$Re(PPh_3)_2$]. It is this 14-electron intermediate that is proposed to be the species responsible for the observed H/D exchange catalysis of **1** and **2**.

Experimental Section

General Procedures. Compound **1** is only slightly air sensitive in the solid state but is unstable in solution toward prolonged exposure to oxygen and moisture. All reactions were performed under vacuum or under a nitrogen atmosphere in a Vacuum Atmospheres Dry-Lab glovebox. All reagents were obtained commercially and put through three freeze−pump−thaw cycles for degassing before use. All deuterated solvents were purchased from MSD Isotopes Merck Chemical Division, distilled under vacuum from dark purple solutions of benzophenone ketyl, and stored in ampules with Teflon-sealed vacuum line adapters. All other solvents were dried similarly and stored in the glovebox.

Proton, carbon, and phosphorus NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer. ^1H NMR chemical shifts were measured in ppm (δ) relative to tetramethylsilane, using the residual ^1H resonances in the deuterated solvents as an internal reference: C_6D_6 (δ 7.15), toluene-d_8 (δ 2.09), and THF-d_8 (δ 3.58). ^{31}P NMR chemical shifts were measured relative to 30% H_3PO_4. Photolyses were carried out by using an Oriel 200 W high-pressure Hg focused-beam lamp fitted with an infrared-absorbing water filter. Additional filters were used to limit irradiation energies as shown in Figure 1 (BP = 365 nm band-pass; LP = 345 nm long pass). Experiments involving more than one sample to be photolyzed under identical conditions were carried out in a merry-go-round apparatus. GC-MS spectra were taken using a Hewlett-Packard 5890 Series II gas chromatograph. Kinetic fits were performed using Microsoft Excel. All errors are quoted as 95% confidence limits ($\pm$(error) = $t\sigma$; σ = standard deviation, t from Student's t distribution).

The synthesis of $CpRe(PPh_3)_2H_2$ was as previously reported.[7] The synthesis of $CpRe(PPh_3)_2HD$ was as for $CpRe(PPh_3)_2H_2$, using $Re(PPh_3)_2D_7$ in place of $Re(PPh_3)_2H_7$.

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Photochemical H/D Exchange Reactions Using CpRe-$(PPh_3)_2H_2$. C_6D_6/THF. Complex **1** (3 mg, 0.0035 mmol) was placed in an NMR tube, and C_6D_6 (0.3 mL) and THF (0.2 mL) were condensed in. The sample was irradiated using a 365 nm BP filter. Examination of the sample by ^1H or ^2H NMR spectroscopy showed the appearance of THF-d_n and $C_6H_{6-n}D_n$. Use of a solvent suppression program allowed the examination of **1**, which showed no evidence of deuterium incorporation into the hydride resonances. A similar experiment was conducted using a C_6H_6 (0.3 mL)/THF-d_8 (0.2 mL) solvent mixture, providing similar results.

C_6D_6/CH_4. Complex **1** (4 mg, 0.047 mmol) and c-C_6D_{12} (2 equiv) were dissolved in 0.4 mL of C_6D_6 in an NMR tube, and 300 equiv of CH_4 was added. The tube was sealed and irradiated using a 365 nm BP filter. A quartet resonance was observed to grow in at δ 0.115 (J = 2.0 Hz) for CH_3D. Integration relative to the c-C_6D_{12} internal standard indicated that 68 turnovers had occurred after 3 h of irradiation.

C_6D_6/C_2H_6. This experiment was performed as for methane, except that 500 equiv of C_2H_6 was used. After 3 h of irradiation the ^2H NMR spectrum showed 33 turnovers of H/D exchange.

C_6D_6/C_3H_8. This experiment was performed as for methane, except that 500 equiv of C_3H_8 was used. Upon irradiation of the sample the ^2H NMR spectrum showed the growth of a septet resonance at δ 0.840 (J = 1.0 Hz) for $CH_3CH_2CH_2D$. A second broad resonance at δ 1.15 was observed for a smaller amount of H/D exchange at the secondary position. Turnover numbers for H/D exchange at various times are given in Table 1.

C_6D_6/c-C_3H_6. This experiment was performed as for methane, except that 1000 equiv of c-C_3H_6 was used. Upon irradiation of the sample the ^2H NMR spectrum showed growth of a broad resonance at δ 0.06 for c-C_3H_5D. Turnover numbers for H/D exchange at various times are given in Table 1.

C_6D_6/c-C_5H_{10}. This experiment was performed as for methane, except that 250 equiv of c-C_5H_{10} was used. Upon irradiation of the sample the ^2H NMR spectrum showed growth of a broad resonance at δ 1.40 for c-C_5H_9D. Turnover numbers for H/D exchange at several times are given in Table 1.

Competitive H/D Exchange. For the competitive H/D exchange studies, 4 mg of **1** (0.0047 mmol), 2 equiv of c-C_6D_{12}, and 0.4 mL of C_6D_6 were placed into an NMR tube along with 100 equiv each of two competing substrates (CH_4/C_2H_6, CH_4/c-C_5H_{10}, or C_6H_6/C_3H_8). The samples were irradiated and the relative rates of reactivity determined by integration of the ^2H NMR spectra after 2 h of irradiation. Relative reactivities are indicated in the text.

Effect of Propane Concentration on H/D Exchange Rate. A stock solution of **1** (0.013 M in THF-d_8 containing 2 equiv c-C_6D_{12}) was prepared and 0.45 mL added to each of three NMR tubes. To each successive tube was added 100, 200, and 300 equiv of propane by condensation. The samples were irradiated through a 365 nm BP filter in a merry-go-round apparatus, and ^2H NMR spectroscopy was used to periodically monitor the H/D exchange. Results are shown in Figure 3.

Phosphine Substitution Concentration Study. Four NMR samples were prepared containing 0.5 mL of a stock solution of **1** in C_6D_6 (5.14×10^{-3} M). To each sample was then added PMe_3, as indicated in Table 2 (as measured by condensation of a known pressure and volume of gaseous PMe_3). The four samples were then irradiated through a 345 nm filter using a merry-go-round apparatus. The phosphine exchange was followed by ^1H NMR spectroscopy by monitoring the ratio of the ortho phenyl protons of **1** and CpRe(PMe_3)(PPh_3)H_2. The kinetic treatment of the data is described in the text.

Comparison of the Rates of H/D Exchange and Phosphine Exchange. A stock solution of **1** in C_6D_6 was prepared (5.14×10^{-3} M), and two NMR samples containing 0.5 mL each were prepared. To the first sample was added 33.8 mg (0.224 M) of PPh_3-d_{15}, and to the second sample was added n-pentane (30 mm vapor, 273 mL, 0.44 mmol = 0.88 M) as a substrate and c-C_6D_{12} (50 mm, 6.41 mL, 6.6 eq) as an internal deuterated standard. The samples were then irradiated through a 345 nm filter using a merry-go-round apparatus. The phosphine exchange was monitored by both ^1H and ^{31}P NMR spectroscopy, while the H/D exchange was monitored by ^2H NMR spectroscopy.

Reaction of CpRe$(PPh_3)_2H_2$ with D_2. A 0.5 mL sample of **1** in C_6D_6 (5.14×10^{-3} M) was placed in an NMR tube. The sample was then placed under 1 atm of D_2 and irradiated through a 345 nm filter. The reaction was followed by ^1H NMR spectroscopy, showing the appearance of resonances at δ 4.29 and −7.95 corresponding to CpRe(PPh_3)$H_{4-n}D_n$.[7]

H/D Exchange Reactivity of 2. Samples containing 1−3 mg of **2** in C_6D_6, methylcyclohexane-d_{14}, n-pentane, THF, pentane/C_6D_6 (1/9, v/v) or pentane/C_6H_6 (1/9, v/v) were irradiated through a 345 nm filter. The reactions were monitored by either ^1H NMR spectroscopy (for those runs using a deuterated solvent) or ^2H NMR spectroscopy (for those runs using a protio solvent). All showed the loss of the Re−D resonance of **2** and the appearance of the Re−H resonance of **1**.

Cyclometalation Experiments. A sample containing **1** in C_6D_6 (5.14×10^{-3} M) and PPh_3-d_{15} (5 mg, 0.036 M) was irradiated for 250 h. Examination of the sample by ^{31}P NMR spectroscopy showed that the initial singlet resonance for PPh_3-d_{15} was supplemented by a series of six smaller downfield singlets corresponding to H/D exchange into the ortho-phenyl positions of the PPh_3-d_{15}. Decomposition of **1** obtained from the sample produced free PPh_3 that also showed evidence of H/D exchange by GC-MS, as peaks were seen at m/e 262−279.

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Supporting Information Available: Tables and figures giving kinetic data for Figures 2−6. This material is available free of charge via the Internet at http://pubs.acs.org.

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