Photochemical C-H Activation and Ligand Exchange Reactions of CpRe(PPh₃)₂H₂. Phosphine Dissociation Is Not Involved

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Received December 4, 1998

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 PMe₃ to give CpRe(PPh₃)(PMe₃)H₂ and then CpRe(PMe₃)₂H₂. Mechanistic studies of these reactions are inconsistent with [CpRe(PPh₃)H₂] as an intermediate. An alternative mechanism is presented proposing that the active species for H/D exchange is the 14-electron cyclic allyl intermediate $[(\eta^3-C_5H_7)Re(PPh_3)_2]$ (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**, $[(\eta^4-C_5H_6)Re(PPh_3)_2H]$ (**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

New York, 1989.

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

$$C_6D_6 + RH \xrightarrow{CpRe(PPh_3)H_2} C_6D_5H + RD$$

$$RH = C_6H_6, CH_4, C_2H_6, C_3H_6, c-C_5H_{10}, THF, Et_2O$$
(1)

or diethyl ether in C₆D₆. 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 PPh₃ to generate the 16-electron fragment [CpRe(PPh₃)H₂], 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)₂H₂.⁶ One observation which did *not* support the proposed mechanism was that the ¹H 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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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 CpReH₂(PPh₃)₂ (1). The reaction of ReH₇(PPh₃)₂ with excess cyclopentadiene in THF yields the η^4 -cyclopentadiene complex (η^4 -C₄H₆)ReH₃(PPh₃)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** (λ > 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 C₆H₆ shows a welldefined absorption maximum at 328 nm ($\epsilon = 1413 \text{ M}^{-1}$ 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 PPh₃ that are produced by the slow photodecomposition of 1. Free PPh₃ ($\sim 1-2\%$) is observed in these samples as the photolysis proceeds. The H/D exchange can be completely inhibited by the addition of free PPh₃ to the initial solution.

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



Figure 1. UV-vis spectrum of **1** in C_6H_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(PPh₃)₂H₂ in C₆D₆^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
5 1		70	74
		120	87
		300	90
THF ^b	6.2	60	488, ^e 840 ^f
		100	520, ^e 895 ^f

^{*a*} [CpRe(PPh₃)₂H₂] = 1.2 mM. ^{*b*} [CpRe(PPh₃)₂H₂] = 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_6D_6 by **1**.

in independent experiments. Figure 3 shows a plot of the H/D exchange between propane and C_6D_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_6D_6 . Irradiation of **1** in the presence of a CH_4/C_2H_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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Figure 3. Effect of propane concentration on H/D exchange with benzene- d_6 catalyzed by 1: (\blacktriangle) 3.84 M; (\blacksquare) 2.56 M; (\blacklozenge) 1.28 M.



Figure 4. Effect of [PMe₃] on phosphine photosubstitution rate: (●) 0.0053 M; (▲) 0.027 M; (■) 0.109 M; (♦) 0.574 M.

Table 2. Effect of [PMe3] on Rates of PhosphinePhotosubstitution in 1

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

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 PMe₃, 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 ¹H NMR spectroscopy by monitoring the ratio of the ortho phosphine protons of **1** with those of the monosubstituted product CpRe(PPh₃)(PMe₃)H₂. Short irradiation times were used to avoid the formation of the disubstituted CpRe(PMe₃)₂H₂. Plots of ln([**1**]/[**1**]₀) vs time are linear, with the slope varying with the concentration of PMe₃ (Figure 4, Table 2).⁸



Figure 5. Dependence of k_{obsd} on [PMe₃] for the photosubstitution of **1**: (a) k_{obsd} vs [PMe₃]; (b) $1/k_{obsd}$ 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

$$\underset{\substack{H^{+} \\ Ph_{3}P}}{\overset{h}{\underset{H}}} \xrightarrow{h_{\nu}} \mathbf{D} \xrightarrow{k_{2}[PMe_{3}]} \underset{\substack{H^{+} \\ Ph_{3}P}}{\overset{h}{\underset{H}}} \underset{\substack{H^{+} \\ Ph_{3}P}}{\overset{h}{\underset{H}}} (2)$$

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) \times

(fraction of **D** that goes on to form **2**)

$$\frac{d[\mathbf{1}]}{dt} = I_0 \frac{[\mathbf{1}]}{[\mathbf{1}]_0} A \Phi_A \frac{k_2 [PMe_3]}{k_{-1} + k_2 [PMe_3]} = k_{obsd} \frac{[\mathbf{1}]}{[\mathbf{1}]_0}$$
(3)

$$k_{\rm obsd} = \frac{k_1 k_2 [\rm PMe_3]}{k_{-1} + k_2 [\rm PMe_3]}$$
(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 PMe₃ 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 PMe₃ on the excited state of **1** would not be expected to show saturation behavior. From eq 4, a plot of $1/k_{obsd}$ 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

⁽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(PPh₃)(PMe₃)H₂ 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., $\Phi_{substitution} \approx 1$), is unlikely in that this would require that the excited state be sufficiently long-lived to undergo bimolecular reaction with PMe₃. 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 C₆D₆ (5.14 \times 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 PPh₃- d_0 (by ¹H NMR spectroscopy). The appearance of free PPh_3 - d_0 is exponential (Figure 6), and fitting to eq 5 gives $k_{obsd} = [1.60(8)] \times$

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

 10^{-5} s⁻¹. The H/D exchange catalysis was followed by monitoring the ratio of the internal standard c-C₆D₁₂ to *n*-pentane-*d* by ²H NMR. The number of turnovers was then calculated as shown in eq 6. A plot of turnover

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

(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, $k_{obsd} = [2.1(4)] \times 10^{-3} \text{ s}^{-1}$ 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.



Reaction of CpReH₂(PPh₃)₂ with D₂. To test for the photodissociation of H₂ from **1**, a sample of **1** in C₆D₆ (5.14 × 10⁻³ M) was placed under an atmosphere of D₂ and the sample irradiated through a 345 nm filter. If H₂ dissociation were occurring, then one would expect to see the rapid formation of CpReD₂(PPh₃)₂ and free H₂. The reaction was followed by ¹H NMR spectroscopy, which showed the slow formation of CpReD_nH_{4-n}(PPh₃), 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 CpReD₂(PPh₃)₂. It therefore seems reasonable that **1** does not lose H₂ upon photolysis.

Preparation and Reactivity of CpReHD(PPh₃)₂ (2). The reaction of ReD₇(PPh₃)₂ with excess CpH at 60 °C results in the formation of CpReHD(PPh₃)₂, as shown in Scheme 2.⁷ The ¹H 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 ³¹P 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 C₆D₆ (5.14 \times 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 ¹H NMR spectrum. A similar experiment in C₆H₆ solvent showed the loss of the Re-D resonance by ²H NMR spectroscopy. Similar observations of the loss of deuteride ligand in 2 were seen upon irradiation in neat C_6D_6 , methylcyclohexane- d_{14} , *n*-pentane, or THF. As mentioned earlier, irradiation of 1 in C₆D₆ 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

⁽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 PPh₃: (a) initial ³¹P{¹H} spectrum of **1** + PPh₃- d_{15} (5 equiv) in C₆D₆ (region shown is for free PPh₃ in solution); (b) ³¹P{¹H} spectrum after 28 h irradiation, showing the formation of PPh₃- d_0 ; (c) ³¹P{¹H} spectrum after 99 h irradiation, showing the formation of PPh₃ 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 PPh₃ ligands. This reaction could then result in the monodeuteration of the PPh₃ 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 PPh₃ 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 PPh₃- d_{15} initially results in the formation of free PPh₃- 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 ³¹P NMR spectroscopy, where there is a monotonic upfield intrinsic isotope shift of ~0.1 ppm per ortho phenyl deuterium exchanged into free PPh₃ (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 CpReH₂(PPh₃)_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 PPh₃ by mass spectroscopy after 250 h of irradiation confirms the presence of d_0-d_{15} isotopomers.

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 -C₅H₅ intermediate (Cp slippage¹⁰) 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-(PPh₃)₂H₂ 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 C₅H₅ ring. Reversible cyclometalation of this species would allow for H/D exchange between the hydride ligand and the orthophenyl of the PPh₃ ligand. This cyclometalated intermediate is similar to the known complex $(\eta^4-C_4H_6)$ Re-(PPh₃)₂H₃, 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 PMe₃ 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 -C₅H₆ 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 -C₅H₆ ligand to generate an η^3 allyl ligand has been seen before in the closely related complex $(\eta^4$ -C₅H₆)ReH₃(PPh₃)₂^{,7} therefore, it is plausible that it could occur in **D** also. In addition, earlier H/D exchange catalysis using Re(PPh₃)₂H₇ 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(PPh₃)H₂D₂ upon irradiation of **1** in the presence of D₂. $(\eta^4$ -C₅H₆)ReH₃(PPh₃)₂ is known to generate CpRe-(PPh₃)H₄ 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.

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 $[(\eta^4 - C_5H_6)ReH(PPh_3)_2]$ is not capable of catalyzing H/D exchange between a solvent and substrate. It can, however, reversibly cyclometalate one of the PPh₃ 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)ReH₃(PPh₃)₂, to form the 14-electron intermediate [(η^3 - C_5H_7)Re(PPh₃)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-pumpthaw 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). ³¹P NMR chemical shifts were measured relative to 30% H₃PO₄. 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(PPh₃)₂H₂ was as previously reported.⁷ The synthesis of CpRe(PPh₃)₂HD was as for CpRe(PPh₃)₂H₂, using Re(PPh₃)₂D₇ in place of Re(PPh₃)₂H₇.

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Photochemical H/D Exchange Reactions Using CpRe-(**PPh₃**)₂**H**₂. **C**₆**D**₆/**THF**. Complex **1** (3 mg, 0.0035 mmol) was placed in an NMR tube, and C₆D₆ (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 C₆H_{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 C₆H₆ (0.3 mL)/THF- d_8 (0.2 mL) solvent mixture, providing similar results.

C₆**D**₆/**CH**₄. Complex **1** (4 mg, 0.047 mmol) and c-C₆D₁₂ (2 equiv) were dissolved in 0.4 mL of C₆D₆ in an NMR tube, and 300 equiv of CH₄ 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 CH₃D. Integration relative to the c-C₆D₁₂ 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 CH₃CH₂CH₂D. 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 (CH₄/C₂H₆, CH₄/ c-C₅H₁₀, or C₆H₆/C₃H₈). 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-C₆D₁₂) 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 \times 10 $^{-3}$ M). To each sample was then added PMe₃, as indicated in Table 2 (as measured by condensation of a known pressure and volume of gaseous PMe₃). 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(PMe₃)(PPh₃)H₂. 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 PPh₃- 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 ³¹P NMR spectroscopy, while the H/D exchange was monitored by ²H NMR spectroscopy.

Reaction of CpRe(PPh₃)₂H₂ with D₂. A 0.5 mL sample of **1** in C₆D₆ (5.14 × 10⁻³ M) was placed in an NMR tube. The sample was then placed under 1 atm of D₂ 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(PPh₃)H_{4-n}D_n.⁷

H/D Exchange Reactivity of 2. Samples containing 1-3 mg of **2** in C₆D₆, methylcyclohexane- d_{14} , *n*-pentane, THF, pentane/C₆D₆ (1/9, v/v) or pentane/C₆H₆ (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 \times 10⁻³ M) and PPh₃- d_{15} (5 mg, 0.036 M) was irradiated for 250 h. Examination of the sample by ³¹P NMR spectroscopy showed that the initial singlet resonance for PPh₃- d_{15} was supplemented by a series of six smaller downfield singlets corresponding to H/D exchange into the ortho-phenyl positions of the PPh₃- d_{15} . Decomposition of **1** obtained from the sample produced free PPh₃ that also showed evidence of H/D exchange by GC-MS, as peaks were seen at m/e 262–279.

Acknowledgment is made to the U.S. Department of Energy, Division of Basic Energy Sciences (Grant No. FG02-86ER13569), for their support of this work.

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.

OM9809872