Table I. Spectral Properties of the Complexes $(RC_5H_4)Fe(CO)_2CH_3$[a]

R	^{29}Si (δ)			^{13}C (δ) SiCH_3			
	α	β	γ	α	β	γ	Fe+CH_3
Me_3Si	-4.1			-0.56			-23.3
Me_3SiMe_2Si	-22.6	-19.0		-3.5	-2.4		-23.1
$Me_3SiMe_2SiMe_2Si$	-19.5	-48.1	-15.1	-2.6	-8.04	-6.7	-22.5
$(Me_3Si)_2MeSi$	-48.2	-15.7		-0.9	-1.37		-22.4
Ph_3SiMe_2Si	-21.5	-22.5		-1.88			-22.5
Ph_3GeMe_2Si	-15.7			-1.52			-22.4
$(CH_3C_5H_4)Fe(CO)_2CH_2Si_2Me_5$	-6.3	-19.9		-1.70	-0.46		-24.0

[a] All the complexes exhibited two CO stretching frequencies at 2010 and 1955 (±1.0) cm^{-1}, and the expected set of ^{13}C resonances for the substituted cyclopentadienyl ring in the range 85-92 ppm. Solvents used were C_6D_6 (NMR) and hexane (infrared).

Table II

	δ($FpSi_n$) - δ($MeSi_n$)			δ(Si_nFpMe) - δ(Si_nMe)		
	α	β	γ	α	β	γ
Me_3Si	41.3			-4.1		
Me_5Si_2	36.5	8.3		-3.2	0.4	
Me_7Si_3	37.2	12.0	0.8	-3.8	0.6	0.0

analyzed by using ^{13}C NMR in both the cyclopentadienyl and methyl carbon regions of the spectra. From such results the following two independent sets of order are obtained: $Fp-SiMe_3 < Fp-Si_2Me_5 \leq Fp-Si_3Me_7 < Fp-SiMe(SiMe_3)_2$, and $Fp-SiMe_2GePh_3 < Fp-SiMe_2SiPh_3$. These aptitudes suggest that both the release of steric contraints at the metal center upon migration, $FpSi_1 < FpSi_3 < FpSi(Si)_2$, and electronic factors, $Fp-SiMe_2GePh_3 < Fp-SiMe_2SiPh_3$, are involved. In the case of the latter two complexes the Si-Fe bond is significantly longer in the disilyl complex than in the silylgermyl complex, 2.346 vs. 2.328 Å, presumably due to the greater electron-donating capacity of the silylgermyl complex.[5,10] This suggests that the stronger Si-Fe bond in the silylgermyl complex results in the poorer migratory aptitude. Bond length data are not available on the other complexes which are, in general, low melting waxes.

Selected spectral data of the new complexes are provided in Table I. All the infrared spectra of the migrated silyl group complexes exhibit two CO stretching bands, at higher frequencies than their parent $Fp-(Si)_n$ complexes, as expected from previous infrared studies on the Fp-C vs. Fp-Si complexes.[6]

A brief mention of the ^{29}Si NMR data is appropriate. Analysis of the chemical shift data is as previously reported,[11] i.e., δ(FpSi) - δ(MeSi) and δ(SiFpMe) - δ(SiMe), Δδ (Table II). Whereas Δδ for Si atoms attached directly to the coordination sphere of the metal via the metal atom are large and positive, +40 ppm, those attached directly via the cyclopentadienyl ligand are small and negative, -4 ppm. The β-Si atom shifts by approximately +11 ppm in the metal attached complexes but is almost unaffected, +0.5 ppm, in the SiFp-Me complexes. In both cases γ-silicon atoms are essentially unaffected by the coordination process as far as chemical shifts are concerned.

We have briefly studied the photochemical properties of the migrated polysilane complexes. There is no evidence for the deoligomerization process noted for the complexes where the silicon chain is directly bonded to the metal atom. Irradiation in the presence of PPh_3 yields the related phosphine-substituted monocarbonyl complexes with the silane chain intact.

Our results show that polysilane chains directly bonded to iron both readily depolymerize and migrate under different reaction conditions and that the depolymerization process is not observed in the migration products. Such chemistry may be of utility in the design of photoresist materials and their development and etching processes.

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Registry No. $Fp-SiMe_3$, 31811-63-9; $Fp-Si_2Me_5$, 53433-61-7; $Fp-SiMe_2SiMe_3$, 56784-37-3; $Fp-SiMe(SiMe_3)_2$, 53433-62-8; $Fp-SiMe_2SiPh_3$, 87882-62-0; $Fp-SiMe_2GePh_3$, 101247-90-9; $(MeC_5H_4)Fe(CO)_2-CH_2SiMe_2SiMe_3$, 101224-82-2; $Fp-SiPh_2Me$, 41619-97-0; $Fp-SiPhMe_2$, 41680-29-9; $Fp-SiPh_3$, 36835-55-9; $(Me_5Si_2C_5H_4)Fe(CO)_2-Me$, 101224-83-3; $Fp-CH_2SiMe_2SiMe_3$, 53695-99-1; $(Me_3SiC_5H_4)Fe(CO)_2CH_3$, 80611-30-9; $(Me_3SiMe_2SiMe_2SiC_5H_4)Fe(CO)_2CH_3$, 101224-84-4; $((Me_3Si)_2MeSiC_5H_4)Fe(CO)_2CH_3$, 101224-85-5; $(Ph_3SiMe_2SiC_5H_4)Fe(CO)_2CH_3$, 101224-86-6; $(Ph_3GeMe_2SiC_5H_4)Fe(CO)_2CH_3$, 101224-87-7.

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Activation of C-H Bonds by Rhenium. Catalytic Intermolecular H/D Exchange with $(\eta^6-C_6H_6)Re(PPh_3)_2H$

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Summary: The complex $(\eta^6-C_6H_6)Re(PPh_3)_2H$ is found to undergo slow photochemical loss of phosphine. The intermediate formed is capable of catalyzing H/D exchange between benzene-d_6 and other arenes in solution as well as with the meta and para hydrogens of the coordinated phosphine ligands. Labeling studies indicate that the simplest oxidative addition/reductive elimination mechanism is not operating in these exchanges.

Many new transition-metal complexes have been discovered during the past 3 years that are capable of activating the C-H bonds in hydrocarbons.[1-11] One class of

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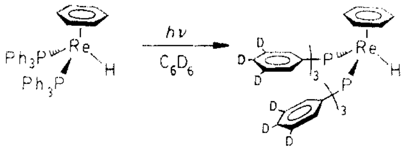
molecules that has been identified for this purpose form electron-rich coordinatively unsaturated intermediates that produce observable oxidative addition adducts with arenes[7-10,12] and alkanes.[6-10] We have recently reported catalytic H/D exchange between alkanes and arenes upon photolysis of $CpRe(PPh_3)_2H_2$[11] and now report isotope exchange studies with the analogous known[13] complex $(\eta^6\text{-}C_6H_6)Re(PPh_3)_2H$ (**1**) involving a mechanism that does *not* exchange the metal–hydride ligand with the deuterium source.

We have found that irradiation of **1** (200-W Hg–Xe lamp, Pyrex filtered) in C_6D_6 solution results in H/D exchange between the benzene solvent and the meta and para positions of the PPh_3 ligands in **1** (eq 1). In a typical experiment 5 mg of **1** in 0.4 mL of benzene-d_6 is irradiated in a sealed NMR tube. The relative areas of the benzene and Re–PPh_3 aromatic resonances are measured by integration of the ^1H NMR spectrum, showing 49% exchange after 15 h, 71% exchange after 33 h, and 98% exchange after 75 h.[14]



(1)

Only the resonance of **1** at δ 6.91 for the combined meta and para hydrogens shows significant exchange relative to the $\eta^6\text{-}C_6H_6$ ligand resonance at δ 4.16. There is evidence for only small quantities of ortho exchange after <3 days of irradiation, implying an intermolecular activation pathway.[15] Furthermore, the hydride resonance relative to the $\eta^6\text{-}C_6H_6$ resonance maintains a 1:6 ratio, and both peaks remain constant relative to silicone grease (δ 0.30) added as an internal standard. Consequently, there can be no exchange of the hydride ligand for deuterium during the PPh_3 H/D exchange reaction. This observation rules out a simple mechanism involving photochemical phosphine loss followed by reversible arene oxidative addition/reductive elimination similar to that proposed for the H/D exchange in Cp_2TaH_3.[16] Such a mechanism would require that deuterium be exchange into the metal hydride position.

Two experiments establish that photolysis of **1** results in phosphine loss.[17] First, irradiation of **1** in the presence of 2 equiv of $P(C_6D_5)_3$ in C_6D_6 solvent shows about 15% phosphine exchange after ~12 h. Second, irradiation of **1** in C_6D_6 under a hydrogen atmosphere (600 mm) for 2–3 days results in the formation of some $(\eta^6\text{-}C_6H_6)Re(PPh_3)H_3$ (30%)[18] and free PPh_3. Both of these observations point toward the formation of the intermediate $[(\eta^6\text{-}C_6H_6)Re(PPh_3)H]$ by what must be rather inefficient PPh_3 and H_2 photodissociation reactions.

Irradiation of two separate solutions of **1** in C_6D_6, one of which also contained 2 equiv of PPh_3-d_{15}, in a merry-go-round apparatus showed 33% H/D exchange of the 18 total meta and para phosphine hydrogens compared with only 15% ligand exchange with PPh_3-d_{15}. H/D exchange was inhibited in the sample containing added PPh_3-d_{15}. The intermediate $[(\eta^6\text{-}C_6H_6)Re(PPh_3)H]$ is therefore rather efficient towards productive H/D exchange, with ~20 full completions of the exchange cycle per dissociation of PPh_3.[19]

Several labeling experiments were used to examine the mechanism of the H/D exchange reaction. First, irradiation of **1** in C_6H_6 under a D_2 atmosphere (530 mm) does not result in the exchange of deuterium into the meta and para phosphine phenyl groups (or the $\eta^6\text{-}C_6H_6$ ring) in **1** (by mass spectroscopy), yet the hydride resonance is observed to disappear due to exchange with deuterium (by ^1H NMR). Mass spectroscopic analysis of the benzene solvent after 7 days of irradiation shows a 4.5% increase in the amount of C_6H_5D in solution (–40 turnovers), indicating that intermolecular H/D exchange between D_2 and benzene is occurring. The ^1H NMR also shows resonances for the formation of a small amount of $(\eta^6\text{-}C_6H_6)Re(PPh_3)D_2H$, formed by photochemical phosphine loss and oxidative addition of D_2.

Second, while irradiation of **1** in C_6D_6 under an H_2 atmosphere results in the formation of some $(\eta^6\text{-}C_6H_6)Re(PPh_3)H_3$ as mentioned above, no exchange of deuterium

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(14) The UV spectrum of **1** displays a well-resolved absorption with λ_{max} = 310 nm. **1**: ^1H NMR (C_6D_6) δ 7.51 (m, 12 H), 6.91 (m, 18 H), 4.16 (s, 6 H. −7.16 (t, J = 36.0 Hz, 1 H).

(15) FDMS of the metal complex after a 7-day irradiation in C_6D_6 shows an approximately Gaussian distribution of mass peaks around *m/e* 804 for **1**-d_{14} with smaller peaks ranging from *m/e* 798 to 810. Longer irradiation times show a distribution skewed toward *m/e* 808 for **1**-d_{18}, although small peaks can be observed up to *m/e* 818 for **1**-d_{28}.

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(18) ^1H NMR (C_6D_6) of $(\eta^6\text{-}C_6H_6)Re(PPh_3)H_3$: δ 7.69 (m, 6 H), 7.02 (m, 9 H), 4.56 (s, 6 H), −7.82 (d, J = 26.4 Hz, 3 H).

(19) After a 5-day irradiation of the sample containing PPh_3-d_{15}, 32% of the Re–H is found to have exchanged for Re–D by ^1H NMR, presumably by way of activation of the PPh_3-d_{15} to make HD, which according to Scheme I would allow formation of Re–D. Turnover number = 18(0.33)/2(0.15) = 20.

Table I. Summary of Labeling Experiment Observations for the Photolysis of 1[a]

expt	results
1. 1 + C_6D_6 + H_2	$C_6D_6 \rightarrow C_6D_5H$ PPh_3-$d_0 \rightarrow PPh_3$-d_n Re–H does not exchange for Re–D
2. 1 + C_6H_6 + D_2	$C_6H_6 \rightarrow C_6H_5D$ PPh_3 does not undergo H/D exchange Re–H → Re–D

[a] Based upon 16 mM 1 under 530 mm H_2 or D_2 gas, irradiated for 160 h.

into the Re–H bond of 1 is observed based upon a 6:1 ratio of the η^6-C_6H_6:Re-H resonances in the ^1H NMR. H/D exchange of the meta and para phosphine phenyl hydrogens does occur slowly (~10% after 40 h), and C_6D_5H is observed to grow in by ^1H NMR spectroscopy (~30 turnovers with respect to 1 after 40 h). The exchange of hydrogen into the benzene-d_6 solvent is qualitatively faster in the presence of hydrogen gas than in its absence. Table I summarizes the results of these reciprocal labeling experiments.

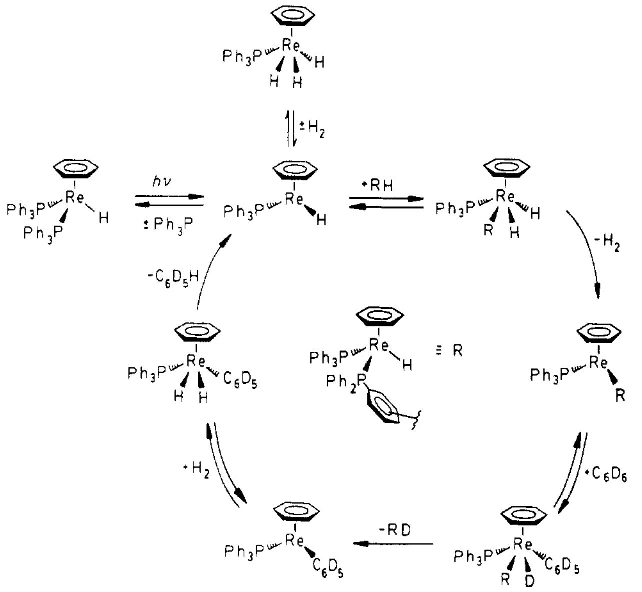
These observations require the following mechanistic features: (1) The hydrogens of the benzene solvent exchange only with the coordinated PPh_3 hydrogens, but not with the hydride ligand of 1. (2) D_2 gas exchanges with the hydride ligand of 1 and with the benzene solvent, but not with the hydrogens of the PPh_3 ligands of 1.

Scheme I shows a proposed mechanism in which three key features follow from the above requirements. First, if R–H (R = $(C_6H_4)Ph_2P$–Re) or benzene adds reversibly to the intermediate [(η^6-C_6H_6)Re(PPh_3)H], it must do so regiospecifically (presumably cis) such that the hydrogen from the aryl group is not equilibrated with the hydride ligand. A similar argument has been made by Curtis for the addition of silanes to Cp_2TaH_3.[20] Second, H_2 addition to the intermediates [(η^6-C_6H_6)Re(PPh_3)R] and [(η^6-C_6H_6)Re(PPh_3)H] must be facile and (η^6-C_6H_6)Re(PPh_3)H_3 must also lose H_2 under the photochemical reaction conditions. Third, the benzene solvent must add to [(η^6-C_6H_6)Re(PPh_3)R] faster than D_2 (at 530 mm); otherwise the phosphine ligand would have been deuterated during the photolysis of 1 in C_6H_6 under a D_2 atmosphere. This requirement is resonable since the benzene is ~12 M whereas the D_2 is <0.01 M.

Scheme I shows all steps as reversible except for the loss of H_2 from [(η^6-C_6H_6)Re(PPh_3)RH_2] and those involving H/D exchange products, since the latter are initially present in small quantities. Also if benzene addition to [(η^6-C_6H_6)Re(PPh_3)R] is rapid, then benzene addition to [(η^6-C_6H_6)Re(PPh_3)(Ph)] should also be rapid, although only a degenerate exchange results. The possible presence of this type of degenerate aryl group exchange means that these experiments therefore serve only to provide a lower limit for the rate of oxidative addition of R–H bonds.

In contrast to CpRe(PPh_3)$_2H_2$,[11] alkanes (methane, propane) do not exchange hydrogen for deuterium in C_6D_6 under these conditions. Other arenes such as toluene do show H/D exchange with C_6D_6. The exchange is limited to only the aromatic hydrogens of the ring, with no benzylic exchange being observed by ^2H NMR.

Scheme I



This system is unique in that all other complexes reported to catalyze arene H/D exchange also exchange deuterium into the metal hydride position.[21] Parshall noted previously that Ta(dmpe)$_2H_5$ also catalyzes deuterium exchange from C_6D_6 into the meta and para positions of PPh_3.[22] Other derivatives of this system are under investigation.

Acknowledgment is made to the U.S. Department of Energy (83ER13095) and to the Camille and Henry Dreyfus and Alfred P. Sloan Foundations for their support of this work. We also thank Prof. R. Eisenberg for helpful discussions.

Registry No. 1, 101519-31-7; [(η^6-C_6H_6)Re(PPh_3)H], 101519-32-8.

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Evidence for a Metallo Ketone Complex in the Reactions of Rhodium Octaethylporphyrin Dimer with Carbon Monoxide: Solution Equilibria and Spectroscopic Studies

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Summary: Proton NMR studies of toluene solutions of rhodium octaethylporphyrin dimer and CO (P_{CO} = 0.2–22 atm) demonstrate the presence of equilibria involving two species with the same stoichiometry (2:1 RhOEP/CO), assigned to an adduct, $(RhOEP)_2(CO)$, and a metallo ke-