

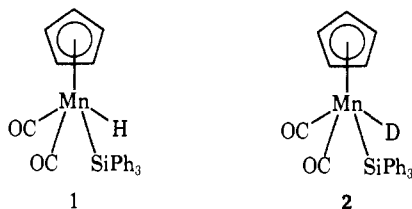
Silicon-Transition Metal Chemistry. VI. Kinetics and Mechanism of the Replacement of Triphenylsilane by Triphenylphosphine in Hydridotriphenylsilyl(π -cyclopentadienyl)dicarbonylmanganese¹

A. J. Hart-Davis and W. A. G. Graham*

Contribution from the Department of Chemistry, University of Alberta,
Edmonton, Alberta, Canada. Received November 13, 1970

Abstract: The kinetics and mechanism of the replacement of triphenylsilane by ligands such as triphenylphosphine from hydridotriphenylsilyl(π -cyclopentadienyl)dicarbonylmanganese (**1**) have been studied in *n*-heptane, toluene, and tetrahydrofuran. The initial process is the rate-determining dissociation of the silane molecule, for which activation parameters (in *n*-heptane) are $\Delta H^\ddagger = 29.2$ kcal/mol, $\Delta S^\ddagger = 16.3$ eu. The reaction is retarded by added triphenylsilane, and competition experiments indicate that triphenylphosphine is 3.6 times as reactive as triphenylsilane toward the intermediate π -cyclopentadienyldicarbonylmanganese. The kinetic isotope effects for both forward and back reactions are small but significant and consistent with the proposed mechanism of a concerted single-stage mechanism for silane dissociation.

The synthesis and some spectroscopic properties of π -C₅H₅Mn(CO)₂HSiPh₃ (**1**) have recently been described, as well as its facile reductive-elimination reac-



tion with triphenylphosphine (eq 1, L = PPh₃).¹ In π -C₅H₅Mn(CO)₂HSiPh₃ + L \longrightarrow π -C₅H₅Mn(CO)₂L + HSiPh₃ (1)

interest in **1** has been heightened by the determination of its structure by X-ray crystallography,² which showed that the unique hydrogen atom, although located at a "normal" distance from manganese, is close enough to silicon to imply some degree of bonding interaction. It thus appeared that **1** provided a simple case of the silicon-hydrogen-transition metal bridges which have been invoked in more complex binuclear derivatives.^{3a} We have accordingly studied the kinetics and mechanism of reaction 1 in an attempt to gain further insight into the nature of the metal-metal and metal-hydrogen bonds.

The reaction is also noteworthy since (a) there appears to have been no previous kinetic study of oxidative addition or reductive elimination involving d⁴ \leftrightarrow d⁶ transformations,⁴ and (b) the reaction which goes to completion is the reductive elimination.

Experimental Section

Materials and General Methods. All operations, including purification of solvents, were carried out under an atmosphere of

(1) Part V: A. J. Hart-Davis, J. K. Hoyano, and W. A. G. Graham, manuscript in preparation.

(2) M. J. Bennett and W. Brooks, manuscript in preparation; *cf.* *Chem. Eng. News*, **48** (24), 75 (1970).

(3) (a) J. K. Hoyano and W. A. G. Graham, *J. Amer. Chem. Soc.*, submitted for publication; **91**, 4568 (1969); (b) W. Jetz and W. A. G. Graham, *ibid.*, **91**, 3375 (1969); *Inorg. Chem.*, **10**, 4 (1971).

(4) J. Halpern, *Accounts Chem. Res.*, **3**, 386 (1970); J. P. Collman, *ibid.*, **1**, 136 (1968); J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 53 (1968).

nitrogen, except where other conditions are specified. The petroleum ether used in this work had bp 37–48°. The solvents *n*-heptane, toluene, and tetrahydrofuran (THF) were fractionated, dried over sodium wire (and, in the case of THF, benzophenone), and distilled from the same drying agent immediately before use. Triphenylphosphine (Strem Chemicals Inc., Danvers, Mass.), triphenylsilane (Pierce Chemical Co., Rockford, Ill.), and triphenyldeuteriosilane¹ were recrystallized twice from petroleum ether; melting points were 79–80, 42.5–43.5, and 42–43.5°, respectively. Phenyl dimethylphosphine was distilled under vacuum before use in kinetic runs. The isotopic purity of the DSiPh₃ was estimated to be 99%.¹

The hydride **1**,¹ the deuteride **2**,¹ MeC₅H₄Mn(CO)₂HSiPh₃,^{3b} C₅H₅Mn(CO)₂HSiCl₃,^{3b} and C₅H₅Re(CO)₂HSiPh₃⁵ were prepared by established procedures, each involving photolysis of the appropriate tricarbonyl compound with the necessary silane. The isotopic purity of the deuteride **2** was estimated to be 98% (see below) and no correction was made for the 2% of **1** impurity when calculating rate constants. The spectra of **1** and **2** have been discussed,¹ and relevant data are: hydride **1** ir (*n*-heptane) 1986 and 1929 cm⁻¹ (ν_{CO}), Raman (solid) 1900 cm⁻¹ (ν_{MnH}); deuteride **2** ir (*n*-heptane) 1985 and 1928 cm⁻¹ (ν_{CO}), Raman (solid) 1355 cm⁻¹ (ν_{MnD}); triphenylsilane ir (*n*-heptane) 2128 cm⁻¹ (ν_{SiH}); triphenyldeuteriosilane ir (*n*-heptane) 1548 cm⁻¹ (ν_{SiD}). No evidence could be found for the presence of any of the trans isomer in solutions of **1** by ir or nmr.¹

Reaction of **1 with Triphenylphosphine.** Compound **1** (93 mg) and PPh₃ (80 mg) were allowed to stand in petroleum ether (100 ml) at room temperature for 3 days. Solvent was removed under vacuum. C₅H₅Mn(CO)₂PPh₃ recrystallized from diethyl ether-petroleum ether as yellow prisms in 60% yield: mp 202–208° (lit.⁶ mp 210–212°); mass spectrum *m/e* (rel intensity) assignment 438 (6) C₅H₅Mn(CO)₂PPh₃, 382 (100) C₅H₅MnPPh₃; ir (*n*-heptane) 1945 and 1885 cm⁻¹, (CHCl₃) 1933 and 1864 cm⁻¹ (lit.⁶ 1934 and 1862 cm⁻¹ (ν_{CO}); nmr (CDCl₃) τ 2.62 (multiplet, 15, Ph), 5.67 (singlet, 5, C₅H₅). *Anal.* Calcd for C₂₅H₂₀MnO₂P: C, 68.5; H, 4.6. Found: C, 68.5; H, 4.7.

Reaction of **1 with Phenyl dimethylphosphine.** Compound **1** (120 mg) and PPhMe₂ (100 mg) were allowed to react in *n*-hexane (40 ml) at reflux temperature for 1.5 hr. Solvent and excess phosphine were removed under vacuum. C₅H₅Mn(CO)₂PPhMe₂ recrystallized from petroleum ether as yellow microcrystals: mp 87–92° (95% yield); mass spectrum *m/e* (rel intensity) assignment 314 (10) C₅H₅Mn(CO)₂PPhMe₂, 258 (100) C₅H₅MnPPhMe₂; ir (*n*-heptane) 1938 and 1876 cm⁻¹ (ν_{CO}); nmr (CDCl₃) τ 2.55 (multiplet, 5, Ph), 5.68 (doublet, 5, $J_{PH} = 2.1$ Hz, C₅H₅), 8.32 (doublet, 6, $J_{PH} = 8.2$ Hz, Me). *Anal.* Calcd for C₁₅H₁₆MnO₂P: C, 57.3; H, 5.1. Found: C, 57.1; H, 5.1.

(5) J. K. Hoyano and W. A. G. Graham, manuscript in preparation.

(6) R. S. Nyholm, S. S. Sandhu, and M. H. B. Stiddard, *J. Chem. Soc.*, 5916 (1963).

Table I. Rates of Reaction of $C_5H_5Mn(CO)_2HSiPh_3$ and Related Compounds with Ligands in *n*-Heptane at 50.1°

$C_5H_5Mn(CO)_2HSiPh_3$			$C_5H_5Mn(CO)_2DSiPh_3$				
L	[L], mM	$10^4k_{obsd}, sec^{-1}$	L	[L], mM	$10^4k_{obsd}, sec^{-1}$		
PPh ₃	8.7 ^a	4.09	PPh ₃	14.0 ^a	4.27		
	16.2	4.21		23.2	4.40 ^b		
	23.3	4.29 ^b					
	32.5	4.19					
	45.2	4.19 ^c					
	58.4	4.28					
	65.7	4.22 ^d					
	25.3	4.67 ^e		66.2	4.25 ^d		
	70.1	4.86 ^e					
	PPhMe ₂	20.6				4.26	MeC ₅ H ₄ Mn(CO) ₂ SHiPh ₃
143.3		4.17					
CO	Ca. 10 (1 atm)	3.7	PPh ₃	68.3	4.3		
DSiPh ₃		45.0					
	<i>a</i>	4.1 ^h					

^a Ligand concentration in these runs was less than ten times that of substrate. ^{b-d} These runs were done in matched pairs. ^e Reaction mixture exposed to overhead lights. ^f Rate of disappearance of infrared band at 640 cm⁻¹ (1.0-mm cells, see ref 1). ^g Rate of growth of ν_{H-SiPh_3} at 2128 cm⁻¹ (1.0-mm cells). ^h Initial rate of decomposition.

Reaction of 2 with Carbon Monoxide. Compound 2 (12 mg) was kept in *n*-hexane (40 ml) at the reflux temperature for 1.5 hr while a slow stream of CO was bubbled through the solution. At the end of this time the infrared spectrum of the reaction mixture showed carbonyl stretching bands of $C_5H_5Mn(CO)_3$ only (ν_{CO} 2028, 1946 cm⁻¹). The solution was then concentrated to ca. 2 ml and a further infrared spectrum taken. From the relative intensities of the bands at 2128 cm⁻¹ (Ph₃SiH) and 1548 cm⁻¹ (Ph₂SiD) and the relative extinction coefficients of these bands (1.2:1) the ratio of concentrations was calculated to be $[Ph_2SiD]/[Ph_3SiH] = 55$. It follows that the isotopic purity of 2 is 98% (with an estimated uncertainty of $\pm 2\%$), and that there is essentially no H-D exchange either during the preparation of 2 or during its reaction with carbon monoxide. The solution was then evaporated to dryness and a mass spectrum of the crude product confirmed the presence of $C_5H_5Mn(CO)_3$ (*m/e* 204) and DSiPh₃ (*m/e* 261) and showed no sign of HSiPh₃. The absence of H-D exchange was also observed qualitatively (by infrared) during reaction of 2 with PPh₃.

Infrared spectra were obtained with a Perkin-Elmer Model 337 spectrophotometer, equipped with a Hewlett-Packard Model 7127A external recorder. Carbonyl peaks were calibrated with CO or DBr and are considered to be accurate to ± 1 cm⁻¹. ¹H nmr spectra were obtained on a Varian A56-60A instrument. Mass spectra were obtained on A. E. I. MS2 and MS12 instruments. Melting points were observed microscopically on a Kofler hot stage.

Kinetic Studies. Kinetics were measured by following the disappearance of the high-energy infrared carbonyl stretching band of the starting material (*e.g.*, 1986 cm⁻¹ for 1 in *n*-heptane), as previously described.⁷ Solutions of 1 in *n*-heptane, toluene, and THF were shown to obey Beer's law. Reaction mixtures were kept in a bath at a constant temperature ($\pm 0.05^\circ$) and samples were removed with a syringe at suitable intervals to determine the infrared spectra. Between 13 and 20 readings were taken during each run. Initial concentrations of substrate were 1.6–3.0 mM in *n*-heptane and 4–12 mM in toluene or THF. Pseudo-first-order conditions, using at least a tenfold excess of ligand, were employed for all the reactions except for those few which are indicated in the tables. These are discussed below. All reactions went to completion. Under kinetic conditions (with a large excess of PPh₃) conversion of 1 to $C_5H_5Mn(CO)_2PPh_3$ was essentially quantitative, as shown by the carbonyl band intensities at zero and infinite time and the relative extinction coefficients of these bands. Except where otherwise indicated (Table I), all flasks were foil wrapped to exclude light.

Excellent straight lines were observed for plots of $\ln(T_0/T)^8$ against time over at least three half-lives of the reaction, showing that the reaction is strictly first order with respect to substrate.

(7) A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, **9**, 2658 (1970).

(8) *T* is the transmittance of the peak being followed and *T*₀ is the transmittance of the base line at that point, determined at "infinite" time.

Table II. Rates of Reaction of $C_5H_5Mn(CO)_2HSiPh_3$ ^a and $C_5H_5Mn(CO)_2DSiPh_3$ with PPh₃ in *n*-Heptane at Different Temperatures

[PPh ₃], mM	$10^4k_{obsd}, sec^{-1}$	[PPh ₃], mM	$10^4k_{obsd}, sec^{-1}$
	25.0°		40.0°
7.6 ^b	0.088	19.6	0.93
{ 20.1	0.083 } ^c	48.0	0.92
{ 21.4	0.090 ^d } ^c	80.7	0.98
{ 39.2	0.084 } ^c		
{ 38.7	0.089 ^d } ^c		
{ 66.4	0.090 } ^c		
{ 66.8	0.089 ^d } ^c		
	31.0°		60.0°
17.2	0.222	26.0	16.9
37.1	0.234	40.6	17.0
56.1	0.225	80.0	17.4

^a All runs refer to the hydride 1 except as noted. ^b Reaction performed under CO atmosphere; combined [L] less than ten times [1]. Products were ca. 70% $C_5H_5Mn(CO)_2PPh_3$ and 30% $C_5H_5Mn(CO)_3$. ^c Values surrounded by braces indicate reactions done in matched pairs (see text). ^d Refers to the deuteride 2.

Rate constants were evaluated from the negative gradients of these lines by a least-squares method. Standard errors⁹ on the gradients were generally less than 1% for runs in *n*-heptane. Typical rate plots are shown in Figure 1. Rate data are recorded in Tables I, II, and III. In some cases the rate of growth of a product band was measured and found in each case to be the same as the rate of disappearance of starting material, showing that the reaction has only one slow step. During the measurement of the kinetic isotope effect for the forward reaction some runs were done in "matched pairs". Reactions of 1 and 2 with PPh₃ (same batch and similar concentrations) were run in *n*-heptane (same batch) at the same time, using identical equipment, taking alternate samples from the two solutions and treating the results by identical least-squares methods. In this way we hoped to eliminate some of the systematic and/or subjective errors which might be expected to interfere with the estimation of a small difference.

Rates of reaction in toluene and THF were rather less precise. In the latter solvent especially there was some decomposition in the later stages of the reactions at 25°, which might be the result of the basicity of the solvent, since the anion $[C_5H_5Mn(CO)_2SiPh_3]^-$ is known⁵ to be unstable. Rate data are recorded in Table IV.

Activation enthalpies were determined from the negative gradients of the plots of $\ln(k_{av}/T)$ against $1/T$, where *T* is the absolute temperature and *k*_{av} is the average value of *k*_{obsd} at that temperature. The results in *n*-heptane gave an excellent linear plot, and the

(9) J. Topping, "Errors of Observations and Their Treatment," IPAPS Monographs for Students, Chapman and Hall, London, 1955.

Table III. Competition Reactions. Rates of Reaction of $C_5H_5Mn(CO)_2HSiPh_3$ (1) and $C_5H_5Mn(CO)_2DSiPh_3$ (2) in the Presence of Added $HSiPh_3$ or $DSiPh_3$ in *n*-Heptane at 50.1°^a

[$HSiPh_3$], mM	[PPh_3], mM	[$HSiPh_3$]/ [PPh_3]	$10^4 k_{obsd}$, sec ⁻¹
23.6 ^b	48.3	0.489	3.94 ^c
31.1	54.4	0.572	3.65
32.5 ^b	32.6	0.997	3.41
66.5 ^b	66.6	0.998	3.56
32.3	32.2	1.003	3.42
67.4	66.6	1.012	3.50
54.0 ^b	45.4	1.189	3.38 ^c
32.0	25.0	1.280	3.22
68.6	36.6	1.874	2.81
55.2	21.2	2.604	2.46
78.7 ^b	26.7	2.948	2.50 ^c
84.9	22.3	3.807	2.09
84.5	19.8	4.268	1.97

^a Values refer to the hydrido compounds except as noted. ^b Reaction with $DSiPh_3$. ^c Reaction with 2 as substrate.

Table IV. Rates of Reaction of $C_5H_5Mn(CO)_2HSiPh_3$ with PPh_3 in Toluene and THF

[PPh_3], mM	$10^4 k_{obsd}$, sec ⁻¹	[PPh_3], mM	$10^4 k_{obsd}$, sec ⁻¹
Toluene, 25.0°		THF, 25.0°	
63	0.092	37	0.16
145	0.086	91	0.11
247	0.078	180	0.14
Toluene, 50.1°		THF, 60.1°	
26	3.2	21 ^a	1.4
72	3.5	21	3.7
172	3.4	42	3.6
		103	4.0
		191	4.6

^a Reaction retarded by $HSiPh_3$ (100 mM).

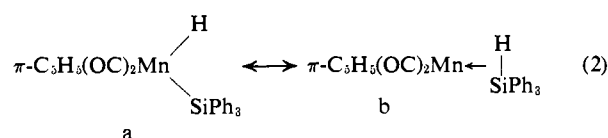
Table V. Activation Parameters for the Reactions of $C_5H_5Mn(CO)_2HSiPh_3$ with PPh_3

Solvent	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
<i>n</i> -Heptane	29.2 (± 0.3)	16.3 (± 1.0)
Toluene	27 (± 1)	9 (± 3)
THF	25 (± 2)	3 (± 6)

standard error on ΔH^\ddagger was only 0.1 kcal/mol. The quoted uncertainties (Table V) may therefore be slightly conservative.

Results and Discussion

A Provisional View of the Bonding in $C_5H_5Mn(CO)_2HSiPh_3$. As noted above, the unique hydrogen atom of 1 was found in the X-ray crystal structure to be "normally" bonded to manganese, but to have a distinct bonding interaction with the silicon atom. One way in which this may be represented is in simple valence-bond terms as a resonance hybrid of two canonical forms. Structure a, which is probably the

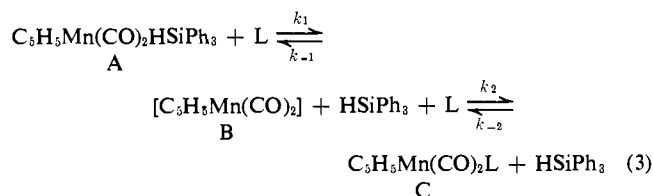


major contributor because of the normal Mn–H bond length, is a hydride of Mn(III), while b is a member of the well-known series of Mn(I) complexes such as $C_5H_5Mn(CO)_2PPh_3$, except that the electrons donated

by L to the manganese atom happen to be a bonding pair in $H:SiPh_3$ instead of a nonbonding pair as in the isoelectronic $:PPh_3$.

Kinetics. The rate data in Table I for the reactions of ligands with 1 in *n*-heptane solution show that the rate of reaction was independent of the ligand and of its concentration, and even with carbon monoxide at a pressure of 1 atm a reasonable rate plot was obtained with a rate constant almost the same as with the phosphines. The reactions with PPh_3 were slightly but significantly faster in the light. The rate of reaction of $MeC_5H_5Mn(CO)_2HSiPh_3$ with PPh_3 was within 10% of that of 1. Table IV shows that the rates were little changed (*ca.* 20%) when toluene or THF was used as solvent, although in the latter there was slight decomposition, so that the rate constants are less precise. Table III shows the effect of triphenylsilane in retarding the reaction. Activation parameters for the different solvents are collected in Table V.

The independence of the rate on the phosphine concentration and the small solvent effect suggest that the reaction is purely unimolecular, with no interference by incoming ligand or solvent before the transition state. The activation parameters, in particular the positive value of ΔS^\ddagger , support a dissociative mechanism. Further the reaction is retarded by triphenylsilane but not by carbon monoxide, and compound 1 reacts with a large excess of $DSiPh_3$ to yield $HSiPh_3$ (and 2) at the same rate as it reacts with PPh_3 . Thus it is reasonable to assume that the overall mechanism is



We assume k_{-2} is negligible, since the reactions go to completion, and the products are known to be inert, at least to ligands such as PPh_3 .^{6,10,11}

Application of the steady-state approximation to the intermediate $[C_5H_5Mn(CO)_2]$ gives

$$\frac{-d[C_5H_5Mn(CO)_2HSiPh_3]}{dt} = k_1[C_5H_5Mn(CO)_2HSiPh_3] \left(\frac{k_2[L]}{k_2[L] + k_{-1}[HSiPh_3]} \right) \quad (4)$$

Provided that $k_2[L] \gg k_{-1}[HSiPh_3]$ this reduces to a pseudo-first-order expression and the observed rate constant is given by

$$k_{obsd} = k_1 \quad (5)$$

Since we observe good first-order rate plots for reactions of 1 with triphenylphosphine this condition must apply even toward the end of the reaction when the triphenylsilane concentration builds up in solution.¹²

If a large excess of triphenylsilane is added to the reaction mixture a pseudo-first-order reaction is still expected, but in this case the observed rate constant is

(10) R. J. Angelici and W. Loewen, *Inorg. Chem.*, **6**, 682 (1967).

(11) R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

(12) From the measured value of 3.6 for k_2/k_{-1} (see below), it follows that with a minimum tenfold excess of PPh_3 the rate after three half-lives will be more than 97% of its original value (k_1). Even in the worst case this drop in rate would hardly be detectable by our method.

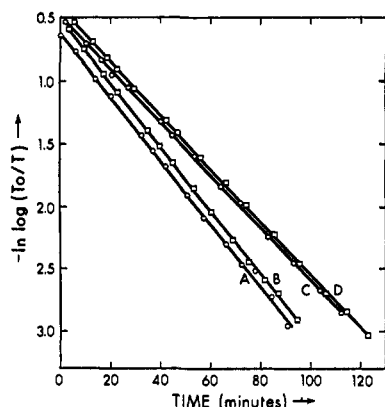


Figure 1. Pseudo-first-order rate plots for reaction of **1** (A, C, and D) and **2** (B) with PPh_3 in *n*-heptane at 50.1° , showing how addition of HSiPh_3 (C) or DSiPh_3 (D) retards the reaction. All PPh_3 and HSiPh_3 or DSiPh_3 concentrations were 66–67 mM.

given by

$$k_{\text{obsd}} = \frac{k_1 k_2 [\text{L}]}{k_2 [\text{L}] + k_{-1} [\text{HSiPh}_3]} \quad (6)$$

A typical rate plot obtained under these conditions is shown in Figure 1C.

Equation 6 may be rearranged to give

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k_1} + \frac{k_{-1} [\text{HSiPh}_3]}{k_1 k_2 [\text{L}]} \quad (7)$$

Thus a plot of $1/k_{\text{obsd}}$ against $[\text{HSiPh}_3]/[\text{L}]$ should give a straight line with an intercept of $1/k_1$. Figure 2A shows such a plot for the data of Table III.¹³ The intercept is 2.3×10^3 sec, in good agreement with 2.36×10^3 sec, the reciprocal of $4.23 \times 10^{-4} \text{ sec}^{-1}$ (k_{av}). From the gradient of the line a value of k_2/k_{-1} may be calculated, which is a measure of the relative reactivities of triphenylphosphine and triphenylsilane toward the intermediate $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2]$. Using the value $k_1 = 4.23 \times 10^{-4} \text{ sec}^{-1}$, $k_2/k_{-1} = 3.6$. The low value of this relative reactivity, in spite of the fact that triphenylsilane is (presumably) a very weak ligand, shows that the intermediate $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2]$ is very reactive and therefore unselective.

A similar kinetic treatment has been presented by Harrod and Smith for the reactions of $\text{HIr}(\text{CO})(\text{PPh}_3)_3$ with silanes.¹⁴ These reactions are essentially the opposite of ours, since triphenylphosphine is replaced by a silane. The mechanism, however, is closely similar, involving dissociation of phosphine followed by uptake of silane by the coordinatively unsaturated intermediate formed. Competition reactions showed that this intermediate, $[\text{HIr}(\text{CO})(\text{PPh}_3)_2]$, reacted 15 times faster with PPh_3 than with HSiPh_3 .¹⁵ It follows that this intermediate is much more selective (and therefore less reactive) than $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2]$, which is reasonable since the chloro analog $\text{ClIr}(\text{CO})(\text{PPh}_3)_2$ is quite stable.

(13) The reagents used in this work are sparingly soluble and slow to dissolve in *n*-heptane. Thus it is difficult to prepare solutions of accurately known concentration. The distinct scatter on the "competition plots" in Figure 2 results from errors on the abscissa, although the errors on individual rate measurements (*i.e.*, the ordinate) were very small (see below). The lines in Figure 2 were calculated by a least-squares method.

(14) J. F. Harrod and C. A. Smith, *Can. J. Chem.*, **48**, 870 (1970).

(15) At 20° in an unspecified solvent, possibly benzene: J. F. Harrod, D. F. R. Gilson, and R. Charles, *ibid.*, **47**, 2205 (1969).

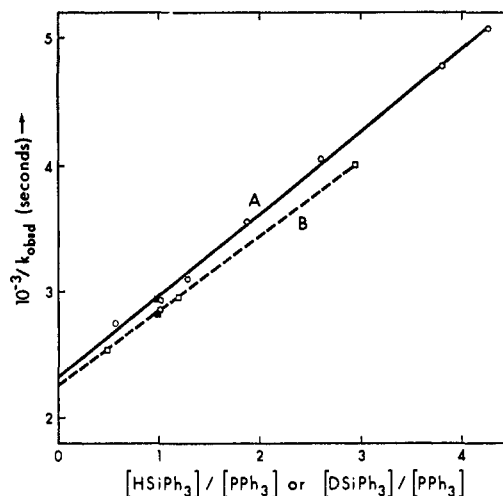


Figure 2. Competition reactions in *n*-heptane at 50.1° . These plots show the linear relationship between $1/k_{\text{obsd}}$ and the relative concentrations of the competing ligands for reactions of **1** (A) and **2** (B): \circ , compound **1** + HSiPh_3 + PPh_3 ; \square , compound **2** + DSiPh_3 + PPh_3 ; \blacksquare , compound **1** + DSiPh_3 + PPh_3 .

We are investigating the possibility of using this competition technique to measure the relative reactivities toward $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2]$ of a number of different ligands, particularly those whose nucleophilicity is generally too low to allow a clean displacement of another ligand (such as CO) from a metal complex.

Kinetic Isotope Effects and the Rate-Determining Step. The deuteride **2** undergoes the same reaction with PPh_3 as the hydride **1** at similar rates. Data for the forward reaction are listed in Table I and give a kinetic isotope effect at 50.1° of $k_{\text{H}}/k_{\text{D}} = 0.97$. Statistically this is probably different from unity,¹⁶ but chemically it is not sufficiently different to show whether or not the hydrogen atom is directly involved during the rate-determining process. Qualitatively, the fact that $k_{\text{D}} \geq k_{\text{H}}$ shows that the hydrogen (or deuterium) atom is bonded at least as strongly in the transition state as in the ground state,¹⁷ so that if the Mn–H bond has been broken at this stage the incipient Si–H bond must be almost completely formed. This is in accord with Hammond's postulate,¹⁸ which predicts that in an endothermic reaction the activated complex will resemble the products rather than the starting materials. Since the dissociation of **1** to give $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2]$ and HSiPh_3 is endothermic,¹⁹ the activated complex may be regarded as a loose combination of $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2]$ with an almost completely formed HSiPh_3 molecule.²⁰

(16) The average values of k_{obsd} for the pseudo-first-order reactions with PPh_3 listed in Table I, and the maximum, average, and root-mean-square deviations from these values are as follows.

	k_{av}	Deviations, %		
		Max	Av	Rms
Hydride 1	4.23	1.2	0.8	0.9
Deuteride 2	4.36	2.6	1.3	1.5

These deviations may be compared with the difference of 3.0% between $k_{\text{av}}(\mathbf{1})$ and $k_{\text{av}}(\mathbf{2})$.

(17) K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955); L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960.

(18) R. O. C. Norman, "Principles of Organic Synthesis," Methuen, London, 1968, p 85.

(19) This may be inferred from the observation that the reaction of $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2]$ with PPh_3 is very fast compared with the rate of dissociation of **1**, and therefore the reaction of $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2]$ with HSiPh_3 , which is only 3.6 times slower than that with PPh_3 , is also much faster than the dissociation of **1**. It follows that the dissociation is endothermic.

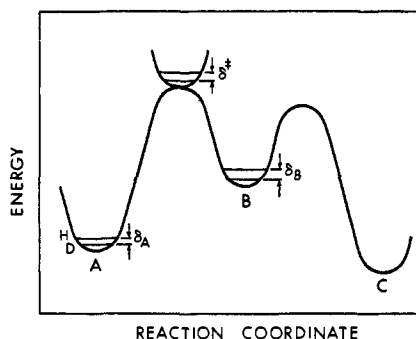


Figure 3. Energy profile for the reaction of **1** with triphenylphosphine according to eq 3.

Quantitatively we may use the observed kinetic isotope effect for the forward reaction to predict a kinetic isotope effect for the back reaction, and compare this with the measured value as a test of the internal consistency of our simple model. We make the approximation¹⁷ that only the difference in zero-point energies associated with the M-H stretching frequencies will affect k_H/k_D . The energy profile of the reaction is illustrated in Figure 3 and the overall mechanism is given in eq 3. Writing δ for the difference in zero-point energies between hydride and deuteride, $\delta = (1/2)h\nu_H - (1/2)h\nu_D$. Using the observed Raman frequencies of $\nu_{Mn-H} = 1900$ (**1**) and $\nu_{Mn-D} = 1355$ cm⁻¹ (**2**) and the infrared frequencies of $\nu_{Si-H} = 2128$ (HSiPh₃) and $\nu_{Si-D} = 1548$ cm⁻¹ (DSiPh₃), we obtain the values $\delta_A = 779$ and $\delta_B = 829$ cal/mol. The measured kinetic isotope effect for the forward reaction $(k_H/k_D)_f = 0.97$ implies a difference in the free energies of activation which is given by

$(\Delta G_H^\ddagger - \Delta G_D^\ddagger)_f = -RT \ln (k_H/k_D)_f = 19$ cal/mol
So the difference in zero-point energies at the transition state is given by

$$\delta^\ddagger = \delta_A + (\Delta G_H^\ddagger - \Delta G_D^\ddagger)_f = 798 \text{ cal/mol}$$

Using this value we may predict the difference in the free energies of the back reaction.

$$(\Delta G_H^\ddagger - \Delta G_D^\ddagger)_b = \delta^\ddagger - \delta_B = -31 \text{ cal/mol}$$

Hence the predicted kinetic isotope effect for the back reaction is given by

$$(k_H/k_D)_b = \exp(\Delta G_H^\ddagger - \Delta G_D^\ddagger)_b = 1.05$$

Figure 2 shows that triphenylphosphine competes slightly more favorably for [C₅H₅Mn(CO)₂] against DSiPh₃ than it does against HSiPh₃. The gradients of the lines in Figure 2 give values for k_2/k_{-1} of 3.62 for HSiPh₃ and 3.83 for DSiPh₃, which yield a kinetic isotope effect for the back reaction (*i.e.*, k_{-1}) of $(k_H/k_D)_b = 1.06$, with an estimated uncertainty of $\pm 2\%$. The excellent agreement between the predicted and observed values, although undoubtedly fortuitous to some extent, supports our contention that the measured kinetic iso-

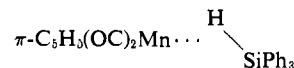
(20) A referee has pointed out that the small kinetic isotope effect observed²¹ for the reactions of H₂ and D₂ with Vaska's compound has been interpreted²² as suggesting little H-H bond breaking in the activated complex. Our conclusions are therefore not without precedent, although the addition of hydrogen to Vaska's compound is not a close analog of our reaction.

(21) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3512 (1966).

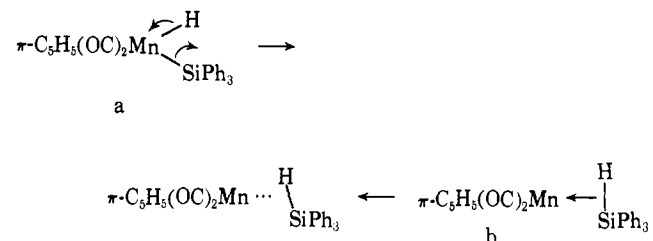
(22) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 53 (1968).

tope effects are significant, in spite of their closeness to unity.

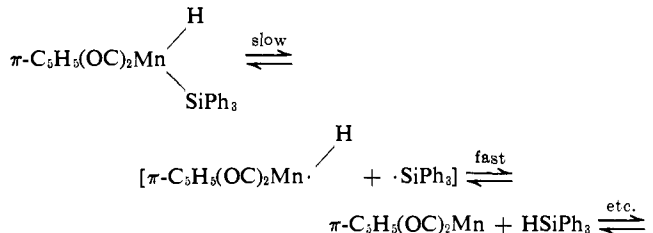
The value of 798 cal/mol calculated for δ^\ddagger suggests that the activated complex may have M-H and M-D stretching frequencies separated by 558 cm⁻¹, *i.e.*, $\nu_{M-H} \approx 2010$ and $\nu_{M-D} \approx 1450$ cm⁻¹, the exact values of which will depend on the isotopic shift in this species.²³ This value of ν_{M-H} seems reasonable for an almost completely formed H-SiPh₃ molecule, and we picture the activated complex in this form.



The angle made by H-Si bond with the Mn \cdots Si axis may range from 0 to *ca.* 90°. This activated complex is readily reached from **1**; in terms of the canonical forms represented in eq 2



This mechanism for the silane dissociation is consistent with all our spectroscopic and kinetic data and probably represents a fair description of events at the molecular level. We cannot, however, entirely rule out a free-radical mechanism involving rate-determining homolytic fission of the Mn-Si bond. We have no evidence for a radical intermediate (the observation of a



paramagnetic terminal product of decomposition¹ does not affect this question). We believe that this radical mechanism is improbable for two reasons. (i) The estimated ν_{M-H} for the activated complex (*ca.* 2010 cm⁻¹) is rather high for an Mn-H stretch (compare values of 1900 in **1** and 1784 in HMn(CO)₅²⁴), and it seems unlikely that the ν_{Mn-H} frequency of **1** could be raised 100 cm⁻¹ merely by stretching the Mn-Si bond, whereas 2010 cm⁻¹ is very reasonable for an almost complete H-SiPh₃ bond. (ii) The back reaction of the radical process must involve the abstraction of a hydrogen atom from triphenylsilane by C₅H₅Mn(CO)₂, which in itself is unexpected, and the isotope effect of this abstraction must retard the *overall* back reaction by only 5%.

(23) The value 558 cm⁻¹ is obtained from the relationship $\delta^\ddagger = (1/2)h(\nu_H^\ddagger - \nu_D^\ddagger)$, assuming once more that all the free energy differences arises from the zero-point energy difference of the M-H and M-D stretching vibrations. The ratio ν_H/ν_D is 1.40 for compounds **1** and **2**, and 1.37 for HSiPh₃ and DSiPh₃. Provided that ν_H/ν_D lies between 1.40 and 1.37 for the activated complex the frequencies will lie between 2066 and 1954 cm⁻¹ (ν_{M-H}) and between 1508 and 1395 cm⁻¹ (ν_{M-D}). Knowing $\nu_H^\ddagger - \nu_D^\ddagger$, we may use an estimated value of the ratio $\nu_H^\ddagger/\nu_D^\ddagger$ to calculate ν_H^\ddagger and ν_D^\ddagger .

(24) W. F. Edgell, J. W. Fisher, G. Asato, and W. M. Risen, Jr., *Inorg. Chem.*, **8**, 1103 (1969).

In conclusion we find the concerted dissociation of silane much more acceptable than a two-stage radical process, although we cannot entirely rule out the latter. The possibility of a concerted process has also been discussed for addition of silanes to $[(\text{diphos})_2\text{Ir}]^+$.²⁵

Decomposition of 1. In *n*-heptane, decomposition of **1** in the absence of added ligand proceeded at the same initial rate as the reaction with ligands. The final carbonyl-containing product was $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$, but intermediate products were formed which will be discussed elsewhere.²⁶

Reactions of Analogs of 1. The compounds $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{HSiCl}_3$ (**3**) and $\text{C}_5\text{H}_5\text{Re}(\text{CO})_2\text{HSiPh}_3$ both undergo analogous silane replacement reactions with PPh_3 , but at very much lower rates. Under conditions similar to those employed for reactions of compound **1** in *n*-heptane, the rhenium analog gave pseudo-first-order rate constants at 150° in decalin of about 10^{-5} sec^{-1} , which is slower than the rate predicted for **1** at that temperature (by extrapolation of the Arrhenius plot) by a factor of more than 10^6 . The trichlorosilyl-manganese compound **3** gave pseudo-first-order rate constants of about 10^{-3} sec^{-1} in decalin at 100° for reaction with PPh_3 , AsPh_3 , or CO or decomposition under nitrogen. The reactions of **3**, however, did not give clean kinetics and we have been unable to obtain reliable data, possibly because of the effectiveness of trichlorosilane as a ligand in competition for $[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2]$.²⁷ It is clear, however, that trichlorosilane is much more firmly attached in **3** than triphenylsilane in **1**. This is in line with the results of Harrod and Smith,²⁵ who showed that silanes dissociated more slowly from an iridium complex as the electronegativity of the substituents on the silicon atom was increased.

(25) J. F. Harrod and C. A. Smith, *J. Amer. Chem. Soc.*, **92**, 2699 (1970).

(26) A. J. Hart-Davis, J. K. Hoyano, and W. A. G. Graham, manuscript in preparation.

(27) Studies of replacement reactions of **3** with the ligands PPhMe_2 and PPh_2Me , which we expected would give cleaner kinetics, were frustrated by the instant precipitation of the salts $[\text{R}_2\text{R}'\text{PH}]^+[\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{SiCl}_3]^-$.²⁸

(28) W. Jetz and W. A. G. Graham, *Inorg. Chem.*, **10**, 1647 (1971).

There are thus three observations concerning compounds **1** and **3** which must be considered.

(i) Compound **1** is known² to have a silicon-hydrogen bridging interaction in the crystal. The silicon-hydrogen distance in **3** is unknown.²⁹

(ii) The manganese-hydrogen stretching vibration of **1** is "silent" in the infrared (*i.e.*, not observed¹), while that of **3** gives a readily observable infrared band. On the other hand, the manganese-hydrogen stretching frequencies of **1** and **3** do not differ significantly.¹

(iii) The activation energy for silane dissociation is much lower for **1** than for **3**.

A considerable difference is expected³⁰ in the electronic properties of the trichlorosilyl and triphenylsilyl ligands, and is reflected, for example, in the carbonyl stretching frequencies of **1** and **3**. Significant differences in the properties of these compounds are therefore to be expected, but as yet we are unable to correlate the three observations above with the properties of the ligands or even with each other. It is tempting to speculate that the facile dissociation of triphenylsilane from **1** is related to the $\text{H} \cdots \text{Si}$ interaction already present in the ground state of the molecule. Whether the infrared silence is also connected with this interaction remains an open question.

We are at present investigating other systems of this nature in order to obtain more information related to these problems. One reason for studying chlorosilyl compounds and their silane replacement reactions is the high silicon-hydrogen stretching frequencies of the parent silanes. This should lead to a greater kinetic isotope effect for either the forward or the back reaction, which would help to justify (or disprove) our quantitative treatment.

Acknowledgment. We thank Professors D. Darwish and R. B. Jordan for helpful discussions and the National Research Council of Canada for financial support.

(29) Crystals of **3** decomposed rapidly in the X-ray beam, so that the crystal structure could not be determined: W. Hutcheon and M. J. Bennett, personal communication. The possibility of a silicon-hydrogen bridging interaction in this compound has been discussed.¹

(30) W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).