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$Mn(CO)_5C(O)$-*p*-$C_6H_5CH_3$-Catalyzed Hydrosilane SiH/SiD Exchange: Evidence from a Kinetics Study Implicating Coordinatively Unsaturated Manganese Silyl Intermediates

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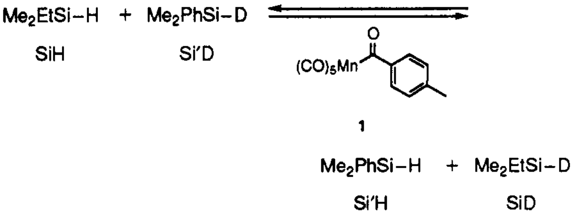
Summary: The manganese p-toluoyl complex $Mn(CO)_5C(O)$-p-$CH_3C_6H_4$ catalyzes SiH/SiD exchange between $DSiMe_2Ph$ and $HSiMe_2Et$ at room temperature in C_6D_6. The preequilibrium kinetics are consistent with a second-order isotope exchange reaction; plots of initial velocities v_0 against $[HSiMe_2Et]_i$ further established saturation kinetics. Lineweaver–Burk plots are in accord with a ping-pong bi–bi mechanism that operates under rapid equilibrium conditions and involves coordinatively unsaturated manganese silyls, $(CO)_4MnSiMe_2R$, as active catalysts.

Hydrosilanes interacting with organotransition-metal silyl and other complexes[1] engender homogeneous catalysts for oligomerizing silanes to polysilanes[2] and hydrosilating organic[3] and organometallic[4,5] substrates. Recent examples include catalyzing the hydrosilation of organic and organometallic acyl carbonyls with manganese carbonyl complexes $Mn(CO)_5Y$.[5c] In studying how these manganese complexes interact with hydrosilanes, we carried out a kinetics study on the manganese *p*-toluoyl complex $Mn(CO)_5C(O)$-*p*-$CH_3C_6H_4$ (**1**)[6] catalyzing SiH/SiD exchange between $DSiMe_2Ph$ and $HSiMe_2Et$ (eq 1).



(1)

In the presence of 0.5–5.0% of **1**, C_6D_6 solutions containing varying ratios of $DSiMe_2Ph$ (Si′D) and $HSiMe_2Et$ (SiH) rapidly equilibrate at room temperature (eq 1). Neither $Mn(CO)_5SiMe_2Ph$ (**2**) nor $Mn_2(CO)_{10}$ catalyzes this hydrosilane exchange.[7] For a given precatalyst (**1**) concentration, these redistribution reactions are characterized by reproducible induction periods of 10–16 min as the initial concentration of SiH was varied by a factor of 12.6. Equilibration requires another 15–22 min;[8] $([SiH]_i - [SiH]_{eq})/[Si'H]_{eq} = 1.4 \pm 0.09\ (2\sigma)$, as $[SiH]_i/[Si'D]_i$ was varied from 0.25 to 4.91.

The induction period corresponds to the reaction of the precatalyst **1** with the hydrosilanes Si′D and SiH (Figure 2). Treatment of **1** with 3–9 equiv of $HSiMe_2Ph$ (Si′H) in independent studies affords the expected[5b] $PhMe_2SiOCH_2C_7H_7$ (**3**) in 93–99% yield by NMR.[9,10] Although we did not detect the α-siloxybenzyl intermediate $Mn(CO)_5CH[OSi(CH_3)_2Ph]$-*p*-$CH_3C_6H_4$,[11] diphenylsiloxy analogs have been identified.[5b,c,e] The manganese silyl byproduct $Mn(CO)_5SiMe_2Ph$ (**2**)[5b] from this reaction was detected only in low yields (19–28%) that decreased with increasing concentration of starting $HSiMe_2Ph$.[12]

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(7) Typical procedure: A C_6D_6 solution (600 mg) containing $HSiMe_2Et$ (51 mg, 0.578 mmol), $DSiMe_2Ph$ (79 mg, 0.578 mmol), $C_6H_5OCH_3$ (10.0 mg, 0.032 mmol) (the internal standard), and then $Mn(CO)_5C(O)C_7H_7$ (**1**) (10.0 mg, 0.032 mmol) was prepared in the glovebox and transferred to a NMR tube, which was capped with a septum. The hydrosilanes had been distilled under nitrogen, and **1** had been freshly recrystallized from methylene chloride/pentane (−18 °C) and vacuum-dried. The light yellow solution was monitored by ^{1}H NMR spectroscopy using delay times and other spectrometer settings that afforded a ±5.0% precision for integrations of the SiH absorptions (δ 4.58 ($HSiMe_2Ph$) 4.03 ($HSiMe_2Et$)). Between 94 and 99% of the starting hydrosilane was accounted for as equilibrium mixtures of $HSiMe_2Ph$ and $HSiMe_2Et$, $([SiH]_{eq} + [Si'H]_{eq})/[SiH]_i$.

(8) Adding more Si′D and SiH to an equilibrated system reinstates the ^{1}H NMR observable exchange reaction. The catalyst mediating this exchange, however, is not a tolerant reagent, and active exchange catalysis rapidly diminishes after about 50 min. Both $Mn(CO)_5C(O)CH_3$ and the bromide $Mn(CO)_5Br$, but not $Mn(CO)_5CH_3$, are viable catalysts of comparable activity for this SiH/SiD exchange. Attempts to use different manganese complexes $Mn(CO)_5Y$ for generating a common active catalyst with constant kinetic properties have been unsuccessful. We have been unable to devise catalysis conditions that minimize the overlap between the induction period (quantitatively generating the active catalyst), the approach to equilibrium (detectable catalysis), and the catalyst degradation.

(9) The isolated yield of **3** after column chromatography on alumina (neutral, activity 3 with CH_2Cl_2–hexane) as a colorless fluid was 86%: ^{1}H NMR (C_6D_6) δ 4.60 (s, $ArCH_2O$), 2.11 (s, $C_6H_4CH_3$), 0.32 (s, $SiCH_3$); ^{13}C NMR δ 65.09 ($ArCH_2O$), 20.09 (s, $C_6H_4CH_3$), −1.51 (s, $SiCH_3$); ^{29}Si NMR ($Cr(acac)_3$) δ 8.04. Anal. Calcd for $C_{16}H_{20}OSi$: C, 74.94; H, 7.86. Found: C, 74.95; H, 7.93. Also detected were the following. (a) $HSiMe_2Ph$: ^{1}H NMR δ 4.58 (sept, J = 3.7 Hz, SiH), 0.23 (d, J = 3.8 Hz, $SiCH_3$); ^{13}C NMR δ −3.79 (s, $SiCH_3$); ^{29}Si NMR δ −16.83. (b) $(PhMe_2Si)_2O$: ^{1}H NMR δ 0.31 (s, $SiCH_3$); ^{13}C NMR δ 0.90 (s, $SiCH_3$); ^{29}Si NMR δ −0.80. (c) $Mn(CO)_5SiMe_2Ph$ (**2**): ^{1}H NMR δ 0.69 (s, $SiCH_3$); ^{13}C NMR δ 4.01 (s, $SiCH_3$); ^{29}Si NMR δ 13.03. Not detected was $(SiMe_2Ph)_2$: ^{1}H NMR δ 0.29 (s, $SiCH_3$); ^{13}C NMR δ −3.83 (s, $SiCH_3$); ^{29}Si NMR δ −21.71.

(10) Both benzyl silyl ethers $C_7H_7CH_2OSiMe_2Ph$ (**3**) and $C_7H_7CH_2OSiMe_2Et$ were independently prepared by $Mn(CO)_5C(O)Ph$-catalyzed hydrosilation of tolualdehyde and were fully characterized.

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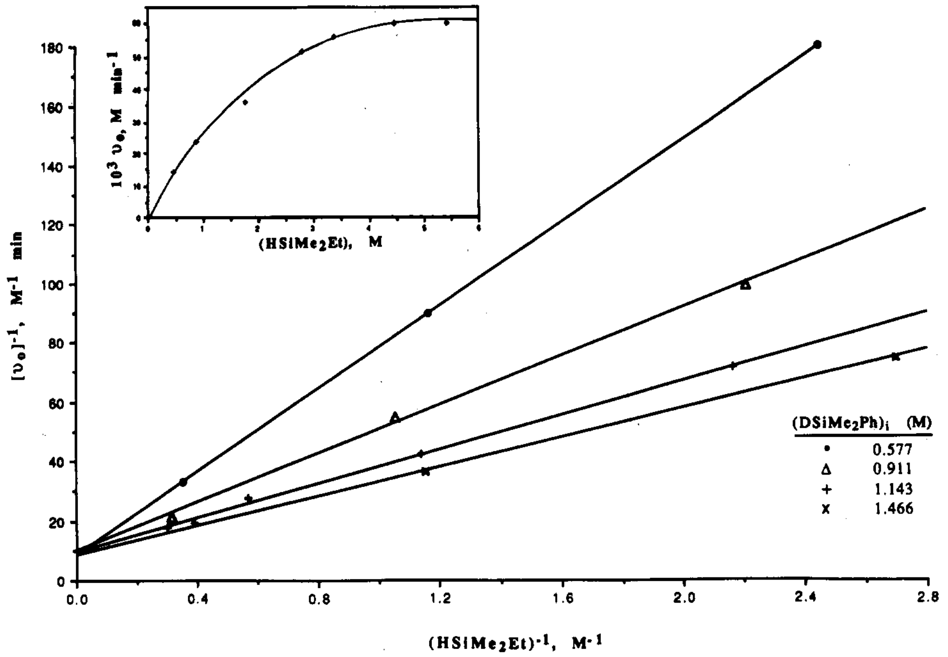

Figure 1. Plots of initial velocities υ_0 vs initial concentrations of varied substrate $HSiMe_2Et$. Initial concentrations: 1 (10 mg), 0.050 M; $DSiMe_2Ph$ (Si′D) (101 mg), 1.143 M; $HSiMe_2Et$ (SiH) (25–300 mg), 0.462–5.409 M; in C_6D_6 (22 °C). The line in the double-reciprocal plot with the smallest slope is for illustration only; it is defined only by two points. Intercept for double reciprocal plots: 8.99 ± 0.75 (2σ).

Results of inhibition studies indicate that adding CO (1 atm) after the induction period has negligible effect, but adding acetonitrile (30 equiv vs 1, 6% vol) stops the exchange. Conducting the SiD/SiH exchange in the presence of air, a potential inhibitor for free-radical reactions, has no effect on the rate or outcome of the reaction. Obvious catalyst degradation (oxidation) to a brown precipitate nevertheless is evident within 45 min, although disiloxanes were not detected (^1H, ^{29}Si NMR).

A kinetics study of this redistribution reaction as it approaches equilibrium[7] agrees with a second-order isotope exchange reaction.[13] Plots of $-\ln[1 - [Si'H]/[Si'H]_{eq}]$ vs time are linear throughout the post-induction preequilibrium period of the reaction; $R^2 > 0.980$ for 16 kinetic runs. Although these linear plots represent a first-order approach to exchange equilibrium, further interpretation of the slope factors requires a starting mechanism and rate law. Fortunately, more definitive mechanistic information was extracted by working with the initial velocities, υ_0, of the exchange reaction.

These initial velocities were determined for constant initial concentrations of precatalyst 1 and Si′D but varying $[SiH]_i$, and plots of υ_0 against $[SiH]_i$ are consistent with saturation kinetics[14] (Figure 1 inset). Further analysis of the data required using double-reciprocal plots of $1/\upsilon_0$ vs $1/[SiH]_i$ (Figure 1).[15] (1) These plots remain linear ($R^2 \geq 0.980$) over wide changes in $[SiH]_i$. (2) The double-reciprocal plots (each line corresponds to a varying concentration of the fixed substrate Si′D) intersect on the vertical axis and pivot clockwise about this point with increasing $[Si'D]_i$. The overall appearance of these double-reciprocal plots, particularly the location of the intersection point, is diagnostic for different bireactant/biproduct pathways.[15]

The presence of an intersection point on the vertical axis of these double-reciprocal plots rules out bireactant pathways that require both substrates SiH and Si′D to simultaneously ligate the active catalyst. These ternary intermediates would derive from ordered or random pathways. Both pathways yield kinetics expressions (using either steady-state or rapid equilibrium approximations) that give double-reciprocal plots exhibiting noncompetitive or mixed-type behavior.[15] Under these conditions, the double-reciprocal plots would intersect to the left of the vertical $1/\upsilon_0$ axis.

Our kinetics data are in accord with a "ping-pong bi–bi mechanism"[16] that operates under rapid equilibrium conditions and uses coordinatively unsaturated manganese

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[11] Johnson and Gladysz generated $Mn(CO)_5CH(OSiMe_3)C_6H_5$ from the reaction between $Mn(CO)_5SiMe_3$ and PhCH(O) at 5 °C (no solvent, 2 weeks). At room temperature, this α-siloxybenzyl complex degrades to the pinacol ether $PhCH(OSiMe_3)CH(OSiMe_3)Ph$ and $Mn_2(CO)_{10}$.[11a] The more stable rhenium α-siloxybenzyl congener was fully characterized.[11b] We found no evidence of this degradation pathway under our reaction conditions. (a) Johnson, D. L.; Gladysz, J. A. *Inorg. Chem.* **1981**, *20*, 2508. Gladysz, J. A. *Acc. Chem. Res.* **1984**, *17*, 326. (b) Selover, J. C.; Vaughn, G. D.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1455.

[12] Isolated yields of 2 after column chromatography on alumina were 19% and 20% for 3.3 and 9.3 equiv of $HSiMe_2Ph$, respectively. Variable amounts of $Mn_2(CO)_{10}$ and $(PhMe_2Si)_2O$ also were detected qualitatively by IR and ^{29}Si NMR spectroscopy. Specifically absent from these reaction mixtures, as determined by ^1H, ^{13}C, and ^{29}Si NMR spectral monitoring, were $(SiMe_2Ph)_2$ and $HSiMePh_2$ or $HSiPh_3$, the potential hydrosilane dehydrogenative coupling and alkyl redistribution products,[2] respectively. Nevertheless, with prolonged reaction times of several hours more $HSiMe_2Ph$ was consumed to give at least three currently unidentified materials.

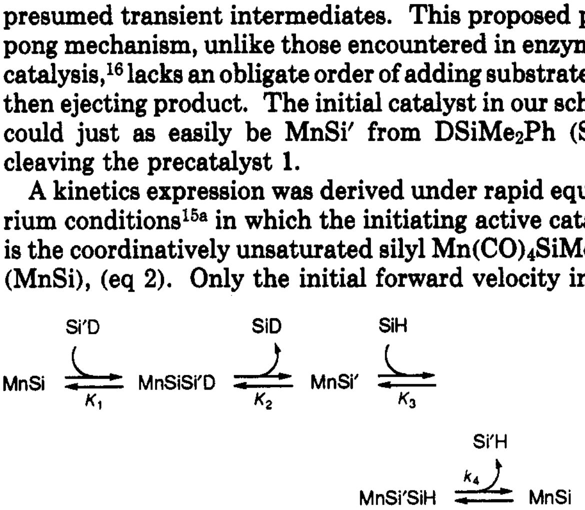
[13] (a) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; pp 50–55. (b) Moore, J. W.; Frost, R. G. *Kinetics and Mechanisms*, 3rd ed.; Wiley: New York, 1986; p 311.

[14] van't Hoff plots, ln υ_0 vs ln $[SiH]_i$ for constant $[Si'D]_i$, show a biphasic dependence of reaction rate on SiH concentration. Although these plots are linear, their slopes depend on the $[Si'D]_i$ that is used for each plot. A similar plot of ln υ_0 vs ln [1] has a slope of 0.42 and $R^2 = 0.970$. This is consistent with a reaction that is half-order in precatalyst 1 with respect to SiH but overall first-order for both SiH and Si′D.

[15] This is the familar Lineweaver–Burk approach for analyzing enzymatic kinetics. (a) Segel, I. H. *Enzyme Kinetics*; Wiley: New York, 1975; Chapters 2–5. (b) Purich, D. L., Ed. *Contemporary Enzyme Kinetics and Mechanism*; Academic Press: New York, 1983; Chapters 1–4, 9, 11. (c) Fromm, H. J. *Initial Rate Enzyme Kinetics*; Springer-Verlag: New York, 1975; Chapters 3–5. (d) Cornish-Bowden, A. *Fundamentals of Enzyme Kinetics*; Butterworths: London, 1979. (e) Cleland, W. W. In *Techniques of Chemistry: Investigation of Rates and Mechanisms of Reactions*; Bernasconi, C. F., Ed.; Wiley-Interscience: New York, 1986; Vol. VI, Part I, Chapter 12.

silyls as active catalysts. These manganese silyls $(CO)_4Mn-SiMe_2Ph$ (MnSi′) and $(CO)_4Mn-SiMe_2Et$ (MnSi) interconvert by sequentially adding one substrate silane and then releasing a product silane. Binary substrate–catalyst intermediates MnSiSi′D and MnSi′SiH (Figure 2) are presumed transient intermediates. This proposed ping-pong mechanism, unlike those encountered in enzymatic catalysis,[16] lacks an obligate order of adding substrate and then ejecting product. The initial catalyst in our scheme could just as easily be MnSi′ from $DSiMe_2Ph$ (SiD′) cleaving the precatalyst 1.

A kinetics expression was derived under rapid equilibrium conditions[15a] in which the initiating active catalyst is the coordinatively unsaturated silyl $Mn(CO)_4SiMe_2Ph$ (MnSi), (eq 2). Only the initial forward velocity in the absence of the second product was considered



(2)

$$v_0 = k_4[\mathrm{MnSi'SiH}] = k_4\frac{K_2[\mathrm{MnSi}][\mathrm{Si'D}][\mathrm{SiH}]}{K_1K_3[\mathrm{SiD}]}$$

and association constants were used. Conservation of manganese species affords

$$[\mathrm{MnSi}]_T = [\mathrm{MnSi}] + [\mathrm{MnSiSi'D}] + [\mathrm{MnSi'}] + [\mathrm{MnSi'SiH}]$$

$$\frac{v_0}{[\mathrm{MnSi}]_T} = \left\{k_4\frac{K_2[\mathrm{MnSi}][\mathrm{Si'D}][\mathrm{SiH}]}{K_1K_3[\mathrm{SiD}]}\right\} \Big/ \left\{[\mathrm{MnSi}] + \frac{[\mathrm{MnSi}][\mathrm{Si'D}]}{K_1} + \frac{K_2[\mathrm{MnSi}][\mathrm{Si'D}]}{K_1[\mathrm{SiD}]} + \frac{K_2[\mathrm{MnSi}][\mathrm{Si'D}][\mathrm{SiH}]}{K_1K_3[\mathrm{SiD}]}\right\}$$

which after collecting the terms gives the final kinetic expression (eq 3). This equation is cast in its double reciprocal form (eq 4)

$$v_0 = \frac{k_4[\mathrm{MnSi}]_T[\mathrm{SiH}]}{K_3\left[\frac{[\mathrm{SiD}]}{K_2}\left\{1 + \frac{K_1}{[\mathrm{Si'D}]}\right\} + 1\right] + [\mathrm{SiH}]} \quad (3)$$

$$\frac{1}{v_0} = \frac{K_3}{k_4[\mathrm{MnSi}]_T}\left[\frac{[\mathrm{SiD}]}{K_2}\left\{1 + \frac{K_1}{[\mathrm{Si'D}]}\right\} + 1\right]\frac{1}{[\mathrm{SiH}]} + \frac{1}{k_4[\mathrm{MnSi}]_T} \quad (4)$$

for graphical analysis as Lineweaver–Burk plots of $1/v_0$ vs $1/[\mathrm{SiH}]_i$. The intercept factor for this equation, $1/(k_4[\mathrm{MnSi}]_T)$, accounts for these plots intersecting on the vertical axis (Figure 1) and affords a value of 133 h^{-1} for the turnover frequency, k_4^{-1}. The competitive activation term, $1 + K_1/[\mathrm{Si'D}]$, verifies that the multiple plots should pivot clockwise about the intersection point with increasing $[\mathrm{Si'D}]_i$.

The efficacy of the precatalyst $Mn(CO)_5Y$ is dictated by how readily it dissociates CO, incorporates hydrosilane, and transforms to the active catalyst. Cis labilization of 1, as established for $Mn(CO)_5Br$[18] and $Mn(CO)_5C(O)CH_3$,[19] promotes CO dissociation; the unsaturated $Mn(CO)_4C(O)C_7H_7$ adds 2 equiv of hydrosilane to give our postulated active catalysts $Mn(CO)_4SiR_3$ (MnSi and MnSi′).[20] These then undergo the oxidative-addition–reductive-elimination steps[1] outlined in Figure 2. A tin analog, $Mn(CO)_4H(SnBu_3)_2$, of the oxidative addition intermediates MnSiSi′D and MnSi′SiH has been identified by Sullivan and Brown[21] as the product of (photochemically generated) $Mn(CO)_4SnBu_3$ and $HSnBu_3$.[22]

Similar oxidative-addition–reductive-elimination steps may account for the reactions of hydrosilanes with $Co(CO)_4SiR_3$, which interchange silyl groups with $HSiR'_3$ and catalyze SiH/SiD exchange.[23] Silyl transfer also occurs by photochemical means[24] and under conditions (<−78 °C) where several examples of $(hydrido)(silyl)_2Co^{III}$ complexes and even the unsaturated $Co(CO)_3SiR_3$ have been detected. In contrast, $RhCl(PPh_3)_3$ catalyzes $HSiEt_3/DSiPh_3$ isotope exchange via a second-order pathway in rhodium.[25]

The proposed intermediates $Mn(CO)_4SiR_3(H)(SiR'_3)$ (e.g., MnSi′SiH) in the catalytic cycle (Figure 2) could describe either oxidative addition or η^2-H–Si binding of the hydrosilane. Both hydrosilane–manganese interactions represent a structure/bonding continuum that has been thoroughly documented for the stable MnCp(L)-

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[16] The usual pattern for a ping-pong bi–bi mechanism entails steady-state conditions for the set sequence for incorporating the initial substrate with a single active site (forward direction). An obligate order or selectivity then exists for the sequence of adding substrate 1 and ejecting product 1 and then adding substrate 2 and ejecting product 2. The resulting kinetic expression therefore defines multiple Lineweaver–Burk plots that that have parallel lines and uncompetitive activation.[15]

[17] The kinetics of our bireactant–biproduct (bi–bi) pathway are linear or pure, on the basis of the appearance of the secondary plot.[15] This replot of the slopes of the Lineweaver–Burk plots, $\mathrm{slope_i}/[\mathrm{SiH}]$ vs $1/[\mathrm{Si'D}]$, is linear ($R^2 = 0.992$).

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[20] Catalyst deactivation entails $Mn(CO)_4SiR_3$ degrading to inactive $Mn(CO)_5SiR_3$. Thus $Mn(CO)_5SiMe_2Ph$ (2) is thermally nonlabile toward either H_2SiPh_2—the corresponding silyl derivative $Mn(CO)_5SiHPh_2$ has been independently characterized[5e]—or PPh_3 at room temperature. Photolysis (5 min) of C_6D_6 solutions of 2 and Si′D/SiH mixtures at 24 °C equilibrates the silanes (eq 1) within 40 min.

[21] Sullivan, R. J.; Brown, T. L. *J. Am. Chem. Soc.* **1991**, *113*, 9155.

[22] Examples of the isolobal analogs $FeCp(CO)H(SiR_3)_2$ and $FeCp(CO)H(SnR_3)_2$ have been reported: (a) Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366. (b) Kawano, Y.; Tobita, H.; Ogino, H. *J. Organomet. Chem.* **1992**, *428*, 125. (c) Reference 4c and others therein. (d) Brunner, H.; Fisch, K. *J. Organomet. Chem.* **1991**, *412*, C11. (e) For Cp*Ru congeners: Straus, D. A.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673.

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[24] (a) Reichel, C. L.; Wrighton, M. S. *Inorg. Chem.* **1980**, *19*, 3858. Anderson, F. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 995. (b) Wrighton, M. S.; Seitz, M. S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 289.

[25] (a) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1976**, *120*, 337. (b) Corriu, R. J. P.; Guérin, C.; Moreau, J. J. E. *Top. Stereochem.* **1984**, *15*, 43.

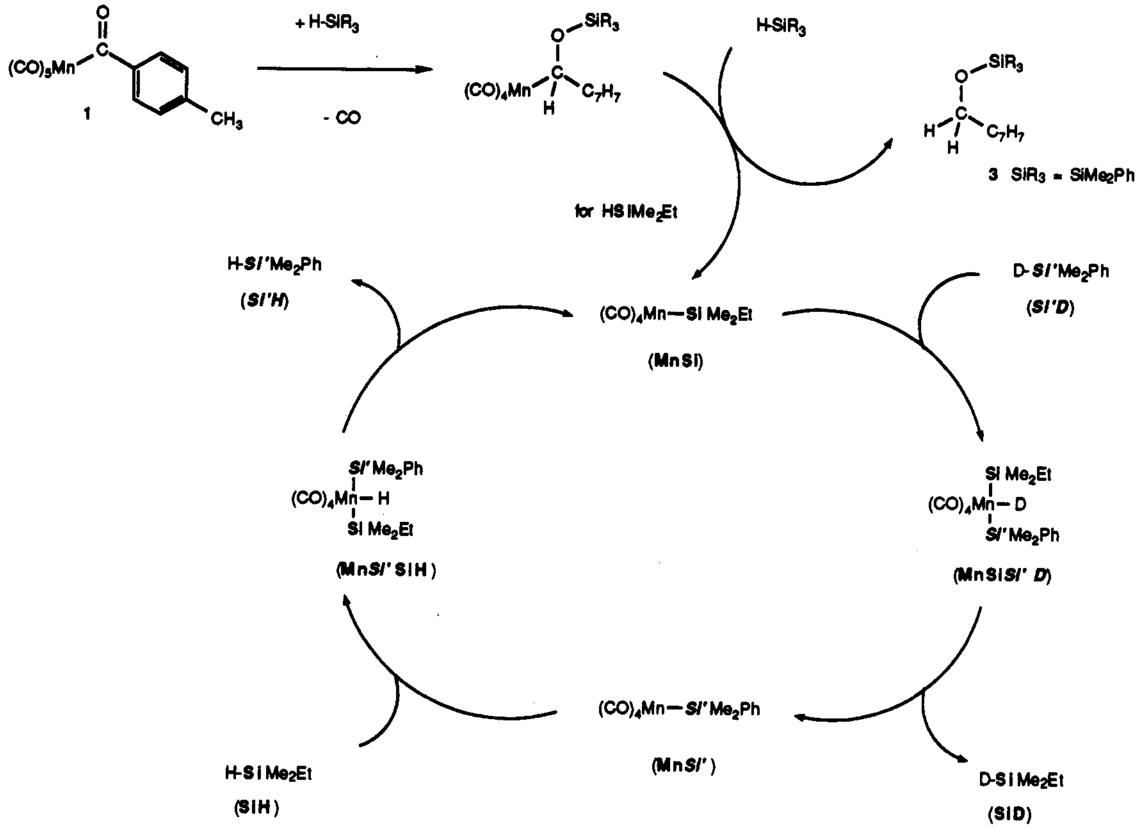

Figure 2. Proposed mechanism for SiH/SiD exchange reaction involving $DSiMe_2Ph$, $HSiMe_2Ph$, and the precatalyst $Mn(CO)_5C(O)C_7H_7$.

$CO(HSiR_3)$ complexes.[26,27] Analogous manganese carbonyl η^2-H–Si hydrosilane complexes could function as reaction intermediates[28] and perhaps promote a σ-metathesis pathway.[2a,29] Ongoing studies will address further characterization of these manganese silyl catalytic systems, particularly with regard to hydrosilation of organometallic acyl complexes, reduction of esters, alcoholysis of hydrosilanes, and dehydrogenative coupling of hydrosilanes.

Acknowledgment. We gratefully acknowledge receiving generous financial support from the Department of Energy, Office of Basic Energy Science.

Supplementary Material Available: Table I, giving kinetics data for SiH/SiD exchange reactions, Figures 3–6, giving double-reciprocal and van't Hoff plots, and Scheme I, giving the derivation of a kinetic expression for a bi-bi ping-pong pathway under rapid equilibrium conditions (9 pages). Ordering information is given on any current masthead page.

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