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^1H NMR Spectral Data for the $(\text{CO})_5\text{MnC}(\text{O})\text{CH}_3$ (2a**)-Catalyzed PhSiH_3 Hydrosilation of $\text{FpC}(\text{O})\text{CH}_3$ (**1a**).**

The chemical shift regions that were assigned for each of **3b-5b** (Table 1) agree with the results of COSY NMR experiments (500 MHz spectrometer). These results helped establish a down-field progression of the methine quartets, the Cp singlets, and the methyl doublets in their ^1H NMR spectra in going from **5b** to **4b** to **3b**. This spectral dispersion is illustrated in Figure 1 (Scan B) for the **2a**-catalyzed PhSiH_3 hydrosilation of **1a**.

The ^1H NMR spectrum of isolated $[\text{FpCH}(\text{CH}_3)\text{O}]_3\text{SiPh}$ (**5b**) is reproduced as Scan C in Figure 1. It resolves four methine quartets between δ 6.20-6.40 (although the overlapping downfield pair are separated by only 2.2 Hz), four Cp singlets, δ 4.41-4.17, and four methyl doublets, δ 2.07-1.97. The results of COSY experiments further correlated these methine and methyl absorptions and were used to assign the four diastereomers labeled A-D in Table 1.

This NMR spectral data are consistent with a constitutionally symmetrical molecule that has three stereogenic FpCHMeO groups branching off of an achiral silicon center. The resulting four stereoisomers constitute a diastereomeric pair of enantiomers [RRR(SSS) and RRS(SSR)].³² Differences in the relative populations of these diastereomers as well as the magnetic (non)equivalency of their FpCHMeO groups accounts for both the presence of four ^1H and ^{13}C NMR spectral signals and their 1:1:1:1 relative intensities for the FpCHMeO groups. For example, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5b** reveals four resonances for the Cp, methine, and methyl absorptions, in addition to eight carbonyl resonances for the diastereotopic $\text{Fe}(\text{CO})_2$ centers.

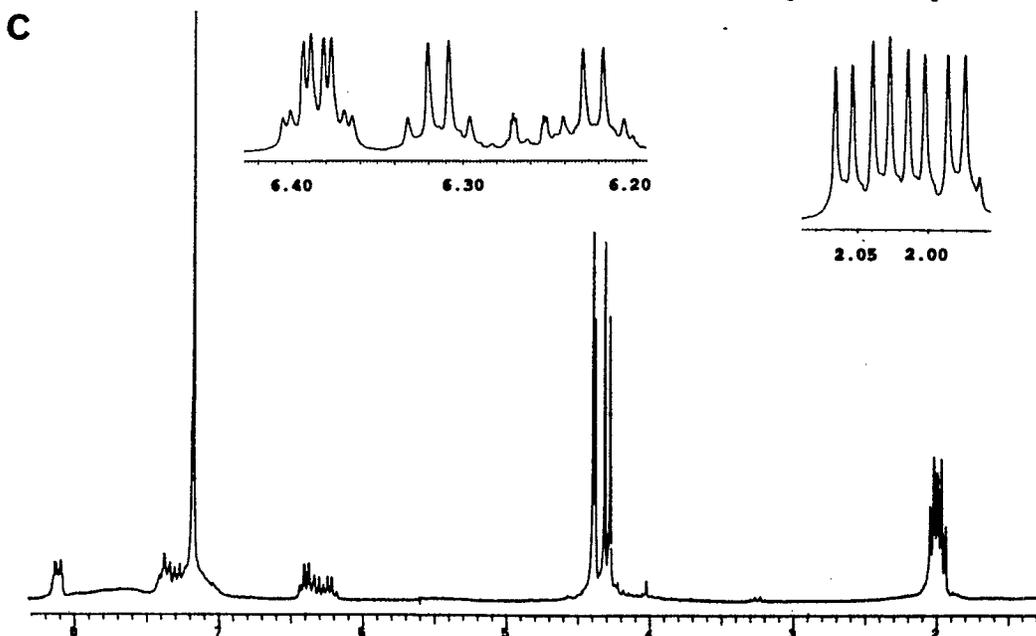
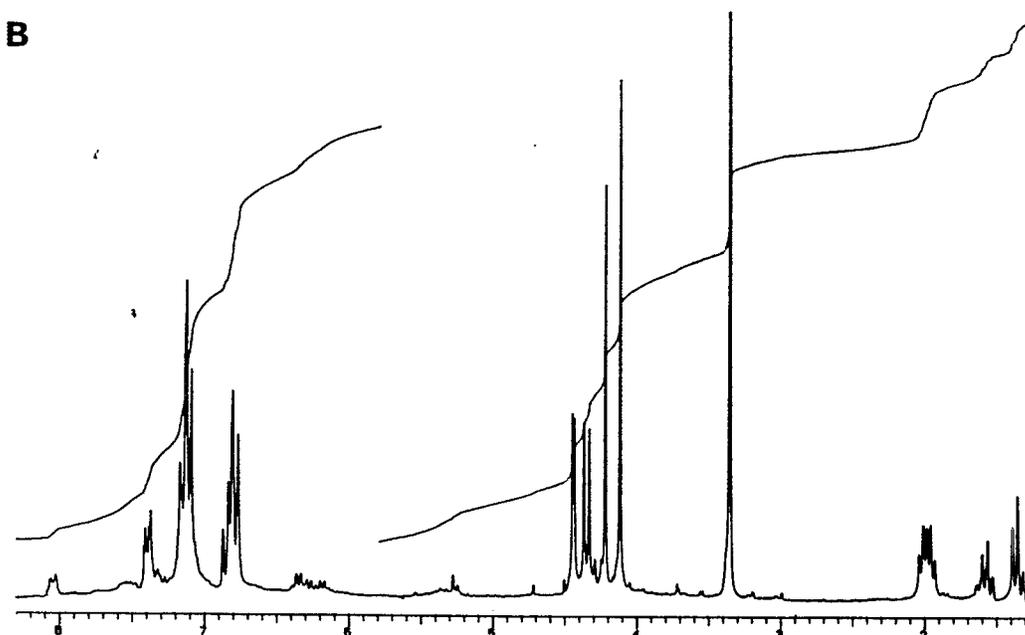
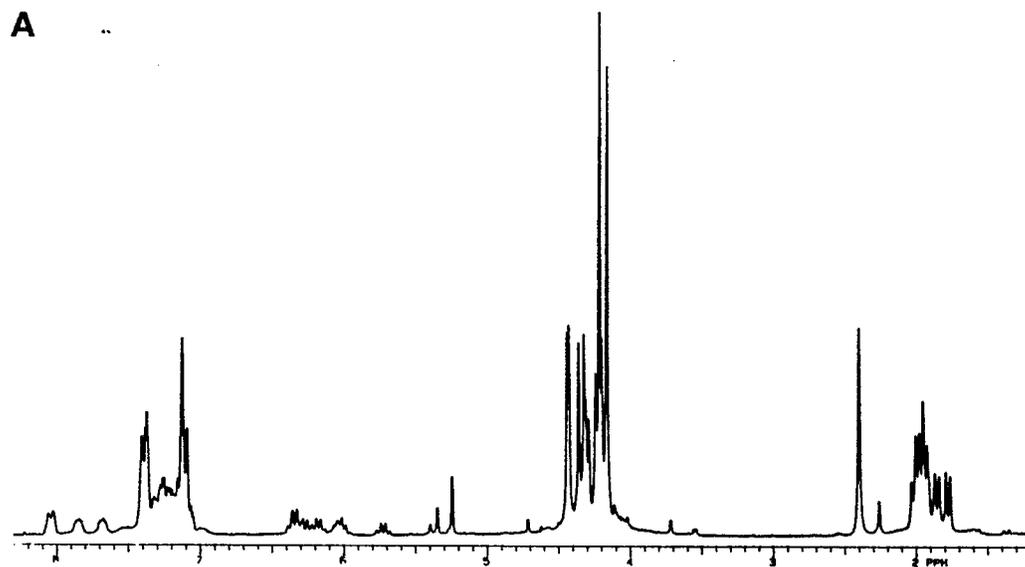
The presence of a C_3 rotational axis on the RRR(SSS) enantiomers of **5b** ensures symmetrically and magnetically equivalent FpCHMeO groups and e.g. a single Cp resonance. Since the RRS(SSR) diastereomers retain three chiral centers that are not related by any symmetry operation, three magnetically nonequivalent FpCHMeO groups, e.g. three Cp resonances, are expected. These diastereomers by virtue of the constitutional symmetry also represent a relative population of six equivalent or enantiomeric stereoisomers vs. the two RRS(SSR) enantiomers, hence the net 1:1:1:1 relative intensities for the Cp (and other FpCHMeO) ^1H and ^{13}C NMR spectral resonances of **5b**.

Figure 1. ^1H NMR Spectra of $(\text{CO})_5\text{MnC}(\text{O})\text{CH}_3$ (2a**)-Catalyzed PhSiH_3 Hydrosilation of $\text{FpC}(\text{O})\text{CH}_3$ (**1a**).**

Scan A (200 MHz) for the reaction mixture of **1a** (0.91 mmol), **2a** (4.6 mol%), and PhSiH_3 (1.09 mmol) in 600 mg of C_6D_6 after 8 h. Intense singlets at δ 4.22 and 4.17 represent unreacted **1a** (also, δ 2.40) and PhSiH_3 , respectively, and the singlet at δ 2.26 pinpoints remaining **2a**. Methine quartets for $[\text{FpCH}(\text{CH}_3)\text{O}]_3\text{SiPh}$ (**5b**) (6.36-6.18) and for $[\text{FpCH}(\text{CH}_3)\text{O}]_2\text{SiHPh}$ (**4b**) (6.07, 6.06) partially overlap, and that of $\text{FpCH}(\text{CH}_3)\text{OSiH}_2\text{Ph}$ (**3b**) is at δ 5.73. The higher field Cp resonances for **4b** (δ 4.31, 4.29) appear as a shoulder on the downfield Cp resonances for **5b** (δ 4.44-4.33); the Cp resonance for **3b** (δ 4.24) overlaps that of **2a**. The upfield methyl doublet of **5b** (δ 2.06-1.98) overlaps the downfield doublet of **4b** (δ 1.93, 1.85); and the methyl doublet of **3b** appears at δ 1.78. Assignments for the methine and methyl ligands were confirmed by COSY NMR experiments.

Scan B (200 MHz) is for a similar reaction mixture after 12 h; anisole (δ 3.35) is present as an internal integration standard. In addition to **5b** and remaining PhSiH_3 , **6a** (δ 4.12, 1.58, 1.35) is clearly evident.

Scan C (200 MHz with 500 MHz insets) of $[\text{FpCH}(\text{CH}_3)\text{O}]_3\text{SiPh}$ (**5b**) after isolation by size exclusion chromatography.



^1H NMR Spectral Data for the $(\text{PPh}_3)(\text{CO})_4\text{MnC}(\text{O})\text{CH}_3$ (2c**)-Catalyzed PhSiH_3 Hydrosilation of $\text{FpC}(\text{O})\text{CH}_3$ (**1a**).**

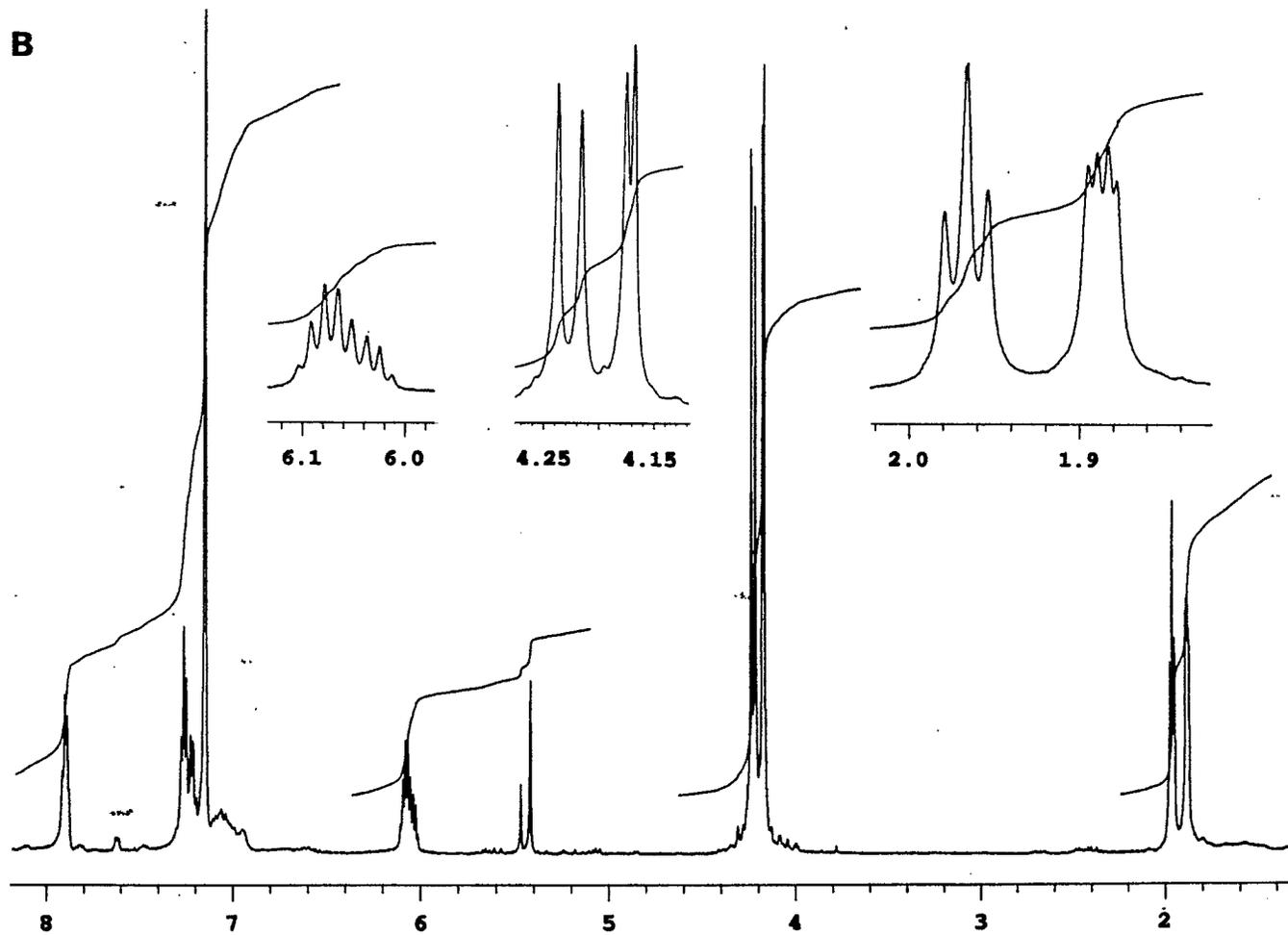
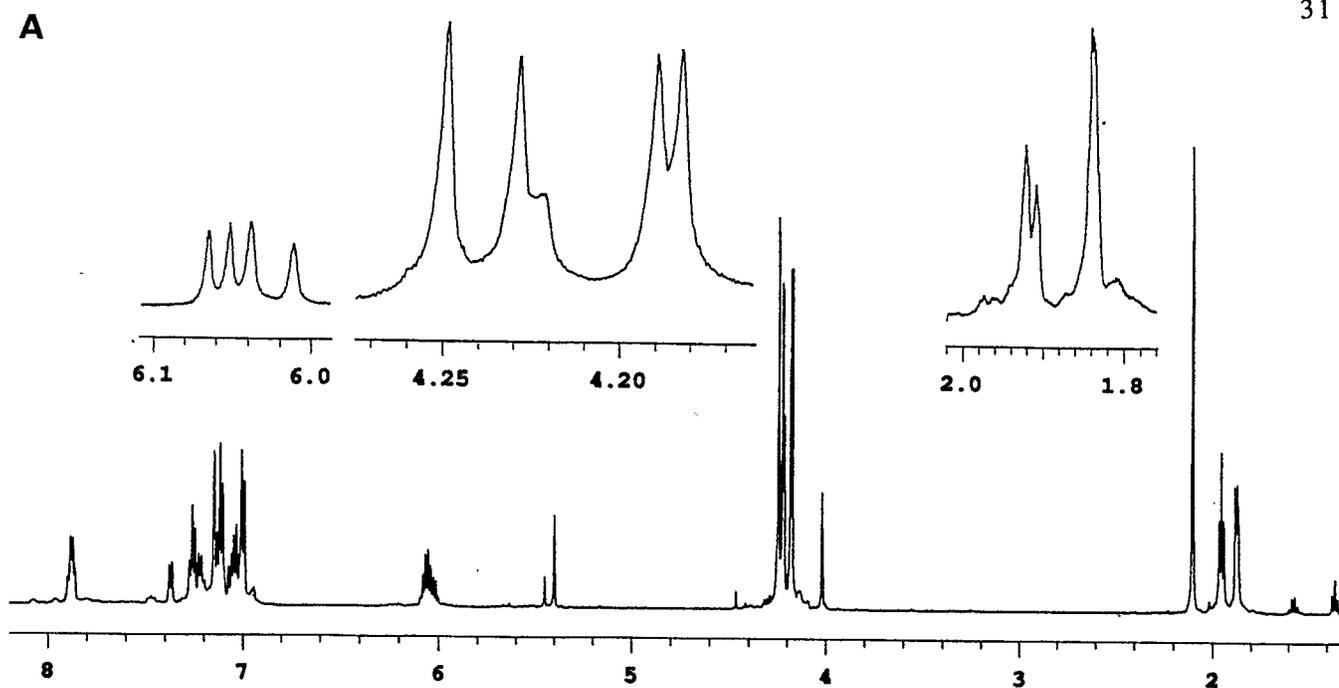
The precatalyst $(\text{PPh}_3)(\text{CO})_4\text{MnC}(\text{O})\text{CH}_3$ (**2c**) differed in activity from **2a** and **2b** in that PhSiH_3 hydrosilation of **1a** yielded $[\text{FpCH}(\text{CH}_3)\text{O}]_2\text{SiHPh}$ (**4b**) as the major product. The use of **2c** (3.0 mol%) as the precatalyst consumed **1a** within 0.5 hour and selectively yielded **4b** and **6a** as the only NMR detectable products. With 0.50 equivalents of PhSiH_3 under otherwise identical conditions, **1a** transformed to mixtures containing 73% **4b** plus 6% **6a**. Figure 2 illustrates the ^1H NMR spectrum for this reaction; the δ 4.3-4.0 region shows the Cp resonances of **4b** (δ 4.25-4.18), the absence of PhSiH_3 (δ 4.22), and the Cp resonance for **6a** (δ 4.02).

An eight-line multiplet appears in the ^1H NMR spectrum of **4b** (500 MHz) at δ 6.10-6.00 that is a composite of four partially overlapping methine quartets. These methine quartets are coupled to the two multiplets that appear for the methyl groups, an apparent triplet at δ 1.96 (which contains two methyl doublets, δ 1.96 and 1.95) and two partially overlapping doublets centered at δ 1.87. COSY NMR experiments further revealed spin correlations between the δ 6.04 and 6.01 methine quartets with the δ 1.96 and 1.95 methyl doublets, and between the 6.07 and 6.05 quartets with the δ 1.88 and 1.87 doublets. HMQC experiments connected these four methyl doublets and four methine quartets with sets of four ^{13}C NMR absorptions between δ 70.20-69.40 and between δ 35.73-35.43, respectively. Although four Cp resonances also were detected in the ^1H NMR spectrum, only three were observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (the δ 86.24 absorption, however, is broadened). The SiH group absorbs as two singlets at δ 5.45 and 5.40 with 1:3 relative intensities.

Figure 2. ^1H NMR Spectra of $(\text{PPh}_3)(\text{CO})_4\text{MnC}(\text{O})\text{CH}_3$ (2c**)-Catalyzed PhSiH_3 Hydrosilation of $\text{FpC}(\text{O})\text{CH}_3$ (**1a**).**

Scan A (500 MHz) for the reaction mixture of **1a** (0.20 mmol), **2c** (3.0 mol%), PhSiH_3 (0.10 mmol), and toluene (0.09 mmol) in 500 mg of C_6D_6 after 0.5 h. The weak singlet at δ 4.22 indicates residual PhSiH_3 , and the absence of singlets at δ 4.17, 2.40 demonstrates that all **1a** has been consumed. Insets show expanded absorptions for $[\text{FpCH}(\text{CH}_3)\text{O}]_2\text{SiHPh}$ (**4b**): Cp region (δ 4.25-4.18); four overlapping methine quartets (δ 6.10-6.00) converted to four singlets after double irradiation at δ 2.1; two partially overlapping methyl doublets (δ 1.96, 1.95) and two methyl doublets (δ 1.88, 1.87) converted to four singlets after double irradiation at δ 6.2.

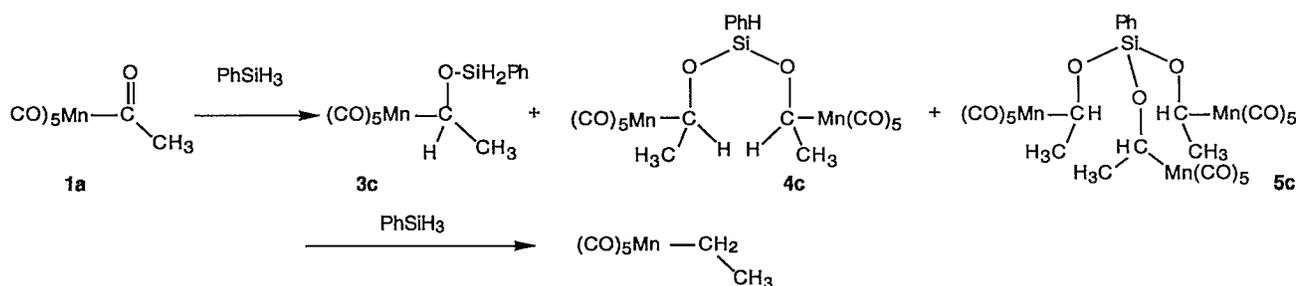
Scan B (500 MHz with expanded insets) of **4b** after isolation by size exclusion chromatography.



Hydrosilation of $(\text{CO})_5\text{MnC}(\text{O})\text{CH}_3$ (**2a**) with PhSiH_3 .

Although the PhSiH_3 hydrosilation of **1a** required the presence of a precatalyst such as $(\text{CO})_5\text{MnC}(\text{O})\text{CH}_3$ (**2a**), this precatalyst largely remained intact until the substrate was consumed. In order to probe this reactivity of **2a**, we briefly studied its hydrosilation by PhSiH_3 . Treatment of **2a** with just one equivalent of PhSiH_3 - no other precatalyst was added - initiated an immediate and exothermic reaction. This reaction consumed all of the manganese acetyl within 15 minutes, as ascertained by NMR spectroscopy. The vigor of this reaction, however, was matched by its product decomposition in these dark brown solutions, and the resulting paramagnetic broadening precluded further analysis of the NMR spectra.

In order to circumvent this decomposition, we studied the PhSiH_3 hydrosilation of **2a** at 5 °C. The substrate was consumed within an hour, and continued NMR spectral monitoring of the orange solutions was possible for several hours before the onset of paramagnetic broadening. These ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectra are consistent with a reaction that converted **2a** to a mixture of $[(\text{CO})_5\text{MnCH}(\text{CH}_3)\text{O}]_x\text{SiH}_{3-x}\text{Ph}$ (**3c**, $x = 1$; **4c**, $x = 2$; **5c**, $x = 3$) and then only slowly to $(\text{CO})_5\text{MnCH}_2\text{CH}_3$ (**6c**) (12%, 2.5 h). The ethoxyphenylsilanes $\text{H}_x\text{Si}(\text{EtO})_{3-x}\text{Ph}$ ($x = 1-3$) were not detected, although over time the reaction mixtures degraded and left moderate yields of $\text{Mn}_2(\text{CO})_{10}$ as the only identifiable organomanganese species.^{1d}



^1H NMR spectra of the **3c-4c-5c** mixtures exhibited complex multiplets at δ 5.49 and 5.27 for methine hydrogens that are coupled to a series of six methyl doublets, δ 1.99-1.82. Five of these methyl doublets are immediately apparent at 500 MHz (confirmed by results of double irradiation of the methine multiplets), and we inferred the sixth from relative intensities as two overlapping doublets at δ 1.99. Other major absorptions were accounted for by a SiH singlet (δ 5.21), unreacted PhSiH_3 (δ 4.22), and the ethyl multiplets for **6c** (δ 1.38, q; 0.93, t, $J = 7.7$ Hz). The ^{13}C $\{^1\text{H}\}$ NMR spectra likewise are dominated by the presence

of closely spaced methine and methyl resonances, δ 69-70 and δ 34-35, respectively, phenyl absorptions, and the ethyl carbons for **6c** (δ 21.06 and 0.05).

Assignment of the mono-, bis-, and tris-manganese α -siloxyethyl complexes **3c-5c** was complicated by the absence of adequate NMR spectral dispersion as was observed for their Fp analogs **3b-5b**. Thus absorptions of **3c-5c** within the methine and methyl chemical shift regions overlap extensively in their ^1H and ^{13}C NMR spectra. Individual methine quartets in the ^1H NMR spectrum of **4c** and **5c** superimpose (even at 500 MHz), and ^{13}C NMR absorptions within the methine and methyl chemical shift regions overlapped to the extent that we only detected four of the methine and five of the methyl resonances.

The results of COSY NMR experiments, however, correlated the methyl doublets with the methine complex multiplets at δ 5.49 and 5.27. Three of the doublets at δ 1.99 and 1.92 couple with the downfield methine multiplet, and the remaining three doublets at δ 1.95, 1.89, and 1.82 correlate with the upfield methine multiplet. We *tentatively* assigned the latter two doublets to $[(\text{CO})_5\text{MnCH}(\text{CH}_3)\text{O}]_2\text{SiHPh}$ (**4c**) on the basis of (a) their relative intensities with respect to the SiH singlet and (b) the upfield chemical shifts of both its methine and methyl absorptions. This NMR spectral data thus represents a 1:1.7 mixture of **4c** and **5c** after 1-2 h.

The hydrosilation of **2a** with PhSiH_3 differed appreciably from those reactions using R_2SiH_2 or R_3SiH , which furnished α -siloxyethyl complexes as the final organomanganese products.¹ With Et_2SiH_2 , for example, mixtures of $(\text{CO})_5\text{MnCH}(\text{OSiHEt}_2)\text{CH}_3$ (**3d**) and $[(\text{CO})_5\text{MnCH}(\text{CH}_3)\text{O}]_2\text{SiEt}_2$ (**4d**) resulted, whereas reactions using Ph_2SiH_2 provided only $(\text{CO})_5\text{MnCH}(\text{OSiHPh}_2)\text{CH}_3$ (**4e**).^{1b} Although unstable, these dihydrosilane adducts of **2a** were unambiguously identified by NMR spectroscopy. [Although the $\text{RhCl}(\text{PPh}_3)_3$ -catalyzed Ph_2SiH_2 hydrosilation of **2a** was reported³ to give **4e**, the presence of $\text{RhCl}(\text{PPh}_3)_3$ is superfluous.] Treatment of **2a** with Me_2PhSiH , on the other hand, afforded the fully characterized $(\text{CO})_5\text{MnCH}(\text{OSiMe}_2\text{Ph})\text{CH}_3$ (eq 1), which is stable in the absence of excess HSiMe_2Ph .^{1d} Its reaction with additional Me_2PhSiH gave degradation product(s) that serve as active catalysts for the hydrosilation of ketones,^{5c} esters,^{5b} **1a**,^{1b,c,e} and even **2a**.^{1d}

Unlike the reaction between **2a** and PhSiH_3 , those using (excess) R_2SiH_2 or R_3SiH do not provide the manganese ethyl complex **6c**.

The hydrosilation of **2a** and its use as a precatalyst for the hydrosilation of **1a** are related.^{1d,e,4a} The observation that most of the precatalyst **2a** remained intact as it promoted the PhSiH_3 hydrosilation of **1a** is consistent with our previously observed hydrosilation chemistry. In kinetics studies to be published, we will document that both **1a** and especially FpC(O)Ph (which is a poor hydrosilation substrate) inhibit the Me_2PhSiH hydrosilation of **2a** as well as the **2a**-catalyzed hydrosilation of **1a**.^{1e}

Hydrosilation of $(\text{CO})_5\text{MnC(O)CH}_3$ (2a**) with PhSiH_3 .** An NMR tube containing 100 mg of **2a** (0.42 mmol) and 45 mg of $\text{C}_6\text{H}_5\text{OCH}_3$ (0.42 mmol) in 600 mg of C_6D_6 was cooled to 5 °C before PhSiH_3 (118 mg, 1.09 mmol) was added by syringe. The resulting light yellow solution turned orange over 1 hour. Within this hour, the starting **2a** was consumed, as determined by ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectroscopy. ^1H NMR double irradiation and COSY experiments of this solution were carried out in order to facilitate the tentative assignments, including that of $(\text{CO})_5\text{MnCH}_2\text{CH}_3$:⁴⁰ ^1H NMR (C_6D_6) δ 1.38 (q, $J = 7.6$ Hz, MnCH_2), 0.93 (t, CH_3); ^{13}C NMR δ 21.06 (CH_3), 0.05 (MnCH_2). $(\text{CO})_5\text{MnCH}(\text{CH}_3)\text{O}_2\text{SiPhH}$ (**4c**) ^1H NMR (C_6D_6) δ 7.91 (m, 2H, Ph-**4c**), 7.30 (m, 2H, Ph-**4c**), 7.22 (m, 4H, Ph-**4c**+**5c**), 5.49 (m, width=90 Hz, MnCH-4c+5c), 5.27 (m, width=80 Hz, MnCH-4c+5c), 5.21 (s, SiH, **4c**), 1.89 (d, $J=5.9$ Hz, CH_3), 1.82 (d, $J=5.9$ Hz, CH_3); ^{13}C NMR δ 212.3 (br s, CO, **4c**+**5c**), 70.05, 69.88, 69.70, 69.34 (MnC , **4c**+**5c**), 35.64, 35.35, 35.06, (CH_3 , **4c**+**5c**), 34.90, 34.81 (CH_3 , **4c**+**5c**). $(\text{CO})_5\text{MnCH}(\text{CH}_3)\text{O}_3\text{SiPh}$ (**5c**) ^1H NMR (C_6D_6) δ 7.76 (m, 2H, Ph-**5c**), 7.22 (m, 4H, Ph-**4c**+**5c**), 5.49 (m, width=90 Hz, MnCH-4c+5c), 5.27 (m, width=80 Hz, MnCH-4c+5c), 1.99 (d, $J=6.3$ Hz, CH_3), 1.99 (d, $J=6.3$ Hz, CH_3), 1.95 (d, $J=6.3$ Hz, CH_3), 1.92 (d, $J=6.3$ Hz, CH_3). Results of COSY experiments: methine multiplet at δ 5.49 correlates with methyl doublets δ 1.99, 1.92 (**5c**), and methine multiplet at δ 5.27 correlates with methyl doublets δ 1.95, 1.99, 1.92 (**5c**).

40. (a) Hieber, W.; Wagner, G. *Ann. Chem.* **1958**, 618, 24. (b) Hieber, W.; Braun, G.; Beck, W. *Chem. Ber.* **1960**, 93, 901. (c) Green, M. L. H.; Nagy, P. L. I. *J. Organometal. Chem.* **1963**, 1, 58.