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Transition Metal Silyl Complexes LVII [1]. Photochemical Reaction of (π-MeC$_5$H$_4$)Mn(CO)$_2$*L* with HMe$_2$Si-*X*-SiMe$_2$H

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Summary. The photochemical reaction of Cp'Mn(CO)$_3$ with HMe$_2$Si-1,2-C$_6$H$_4$-SiMe$_2$H and of Cp'Mn(CO)$_2$PMe$_3$ with HMe$_2$Si-X-SiMe$_2$H (X = 1,2-C$_6$H$_4$, C$_2$H$_4$, O) results in the formation of the oxidative addition products Cp'(CO)(L)Mn(H)SiMe$_2$-X-SiMe$_2$H. Except for the combination X = 1,2-C$_6$H$_4$ and L = PMe$_3$, the binuclear complexes [Cp'(CO)(L)Mn(H)SiMe$_2$]$_2X$ are additionally formed.

Keywords. Metal Silyl complexes; Oxidative addition; Hydride complexes.

Übergangsmetall-Silyl-Komplexe, 57. Mitt. [1]**. Photochemische Umsetzung von (π-MeC$_5$H$_4$)Mn(CO)$_2$*L* mit HMe$_2$Si-*X*-SiMe$_2$H**

Zusammenfassung. Photochemische Umsetzung von Cp'Mn(CO)$_3$ mit HMe$_2$Si-1,2-C$_6$H$_4$-SiMe$_2$H und von Cp'Mn(CO)$_2$PMe$_3$ mit HMe$_2$Si-X-SiMe$_2$H (X = 1,2-C$_6$H$_4$, C$_2$H$_4$,O) führt zur Bildung der oxidativen Additionsprodukte Cp'(CO)(L)Mn(H)SiMe$_2$-X-SiMe$_2$H. Außer bei der Kombination X = 1,2-C$_6$H$_4$ und L = PMe$_3$ werden auch die zweikernigen Komplexe [Cp'(CO)(L)Mn(H)SiMe$_2$]$_2X$ gebildet.

Introduction

One possible route to transition metal *bis*(silyl) complexes L_nM(SiR_3)$_2$ is the reaction of hydrido silyl complexes L_nM(H)SiR_3 with hydrogenosilanes HSiR_3. Although there are several examples, only little is known about the factors governing this reaction. It is only observed for certain L_nM/SiR_3 combinations. In the (CO)$_3$(L)Fe(H)SiR_3/HSiR_3 system (L = CO, PR_3) [2], the formation of *bis*(silyl) complexes is disfavoured by electron donating ligands L and favoured by silyl groups with electronegative substituents R such as SiCl$_3$. Other transition metal hydrides also react with silanes. Thus, silanes and d^0 metal complexes, including some lanthanide hydrides, undergo, σ-bond metathesis to form metal silyl complexes [3]. The requirements for the metal center in hydrido silyl complexes L_nM(H)SiR_3 to form *bis*(silyl) complexes upon reaction with HSiR_3 are not yet clear. There may be even different mechanisms (oxidative addition/reductive

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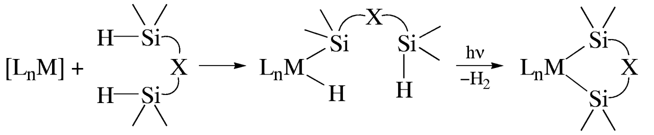
elimination or σ-bond metathesis) requiring different properties of the metal center. Furthermore, compensation effects cannot be ruled out, because in all known examples the residues R of the silyl ligand in $L_nM(H)SiR_3$ are the same as in $HSiR_3$. Increasing the acidity of $HSiR_3$ leads to more acidic hydrido silyl complexes $L_nM(H)SiR_3$.

Whereas the role of the metal center in these reactions is not clear, it is evident that the reaction is favoured by a higher acididy of the silane. This is also supported by the observation that this reaction is more often observed for hydrogenostannanes ($HSnR_3$) than for the corresponding silanes. For example, whereas $Cp'(CO)_2Mn(H)SnPh_3$ ($Cp' = \pi\text{-}MeC_5H_4$) readily reacts with $HSnPh_3$ at room temperature to give *trans*-$Cp'(CO)_2Mn(SnPh_3)_2$ and H_2 [4], there is no reaction between $Cp'(CO)_2Mn(H)SiPh_3$ and $HSiPh_3$ [5].

It is known that chelate assistance promotes oxidative addition reactions. For hydrogenosilanes this has been demonstrated by *Stobbart et al.* [6] who have used $R_2P(CH_2)_nSiR'_2H$. After coordination of the phosphorus center to the metal, the oxidative addition of the Si-H bond is favoured relative to the corresponding non-chelating situation. We have recently shown that chelate assistence also promotes the oxidative addition of bonds which less readily undergo this reaction, such as Si-Si, Sn-C, or Si-C bonds [7].

Chelate assistance may also promote the formation of *bis*(silyl) complexes. The question whether silanes of the type $HR_2Si\text{-}X\text{-}SiR_2H$ undergo the "backbiting" reaction generally shown in Eq. (1) is an important issue in the metal catalyzed formation of polysilanes from H_2SiR_2. In this case, the spacer X would be $(SiR_2)_n$, and the formation of cyclic *bis*(silyl) complexes could lead to the unwanted cyclosilanes.



(1)

There are several examples for the formation of cyclic *bis*(silyl) complexes from $HR_2Si\text{-}X\text{-}SiR_2H$ with $X = 1,2\text{-}C_6H_4$, C_2H_4, and O [8]. In most of these cases reactive metal complex fragments were employed. Comparable reactions with non-chelating silanes $HSiR_3$, if known, proceed less readily. We wanted to test the possibility of a chelate assisted formation of *bis*(silyl) complexes for a metal fragment which is rather unfavourable for this reaction in order to get a feeling about the magnitude of the chelate effect.

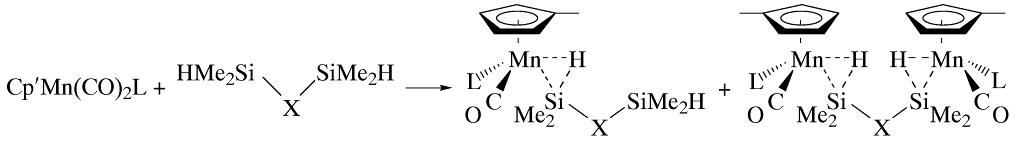
Bis(silyl) complexes $Cp'(CO)_2Mn(SiR_3)_2$ can only be obtained from $Cp'(CO)_2Mn(H)SiR_3$ and $HSiR_3$ with strongly acidic silanes such as $HSiCl_3$ or $HSiMeCl_2$, but not, as mentioned above, with trialkyl or triarylsilanes [4]. In these complexes, the silyl ligands are oriented trans to each other, an unfavourable situation for cyclic *bis*(silyl) complexes. A *cis*-configurated *bis*(silyl) complex was only obtained by oxidative addition of 1,1,2,2-tetrafluoro-3-tert.butyl-1,2-disilacyclobutene to the $Cp'Mn(CO)_2$ fragment [9]. We have previously shown that the SiH end of the hydrido disilanyl complexes $Cp'(CO)_2Mn(H)SiPh(R)\text{-}SiH(Ph)R$ (R = Me, Ph) does not react with the MnH bond to give a cyclic product (which in this particular case would have been a disilene complex) [10]. The goal of the present study was to test whether a larger ring size could favour this reaction.

Results and Discussion

When *Cp*′Mn(CO)$_3$ was irradiated together with an excess of 1,2-*bis*(dimethylsilyl) benzene in petroleum ether at -20°C, vigorous gas evolution started after few minutes. New CO bands appeared at 1980 and 1917 cm^{-1} in the IR spectrum. The solution was irradiated until the gas evolution ceased and the intensity of the CO bands no longer increased. In all reactions described in this paper the turnover was incomplete, even after prolonged irradiation periods and with a large excess of the silane.

The new CO bands were in the same range as those of known hydrido silyl complexes of this type, such as *Cp*′(CO)$_2$Mn(H)SiMePh$_2$ (1984 and 1924 cm^{-1}) [11]. The intensity ratio of the two CO bands showed that the CO ligands are in a *cis* disposition.

The ^{1}H NMR spectra were difficult to interpret because of partial overlap of the signals. A spectrum taken from the reaction solution showed the signal of a Si-H group. It is shifted to lower field by 0.5 ppm relative to the parent silane. Whereas only one new SiH signal was observed, there were two hydride signals at -12.3 and -11.7 ppm with an approximate intensity ratio of 3:1. This indicated the formation of both a mono-(**1a**) and a dinuclear (**1b**) manganese complex (Eq. (2)). The two compounds could not be separated due to their thermal instability and their similar solubility. There was no indication for the formation of a *bis*(silyl) complex.



(2)

$$X = 1,2\text{-}C_6H_4, \quad L = CO: \quad \mathbf{1a} + \mathbf{1b}$$
$$X = 1,2\text{-}C_6H_4, \quad L = PMe_3: \quad \mathbf{2a}$$
$$X = C_2H_4, \quad L = PMe_3: \quad \mathbf{3a} + \mathbf{3b}$$
$$X = O, \quad L = PMe_3: \quad \mathbf{4a} + \mathbf{4b}$$

The stability of the complexes should be higher when the electron density at the metal is increased. When the solution of *Cp*′Mn(CO)$_2$PMe$_3$ and an excess of 1,2-*bis*(dimethylsilyl) benzene were irradiated at 0°C, the IR spectrum of the reaction solution after 12 h showed the bands of *Cp*′Mn(CO)$_2$PMe$_3$, *Cp*′Mn(CO)(PMe$_3$)$_2$, *Cp*′Mn(CO)$_3$, **1a**, and **1b**. *Cp*′Mn(CO)$_3$ is formed by CO elimination from *Cp*′Mn(CO)$_2$PMe$_3$, and *Cp*′Mn(CO)(PMe$_3$)$_2$, **1a**, and **1b** by the reaction of *Cp*′Mn(CO)$_3$ with the liberated PMe$_3$ or the silane [12]. The product **2a** displays a CO band at 1871 cm^{-1} which overlaps with the CO band of *Cp*′Mn(CO)$_2$PMe$_2$ at 1881 cm^{-1}.

The ^{1}H NMR spectrum of the reaction mixture shows that only the mononuclear complex **2a** was formed. The oxidative addition of a second *Cp*′(CO)(PMe$_3$)Mn fragment to the rather rigid *ortho*-*bis*(silyl) benzene probably is no longer possible because of the increased size of the metal complex fragment. Similar results were obtained upon reaction of *Cp*′Mn(CO)$_3$ with HMe$_x$Ph$_{2-x}$Si-

$SiMe_xPh_{2-x}H$ where the tendency to form the dinuclear complexes $[Cp'(CO)_2Mn(H)SiR_2]_2$ decreases with decreasing x [10].

Yellow crystals precipitated within two days at −25°C from the reaction mixture which were identified as the mononuclear complex **2a**. This compound is even stable in air for a short period. The $^{29}Si\ \{^1H\}$NMR spectrum showed two signals, a doublet at 26.1 ppm ($J_{PMnSi} = 7.3$ Hz) and a singlet at −24.2 ppm. The doublet was assigned to the metal bonded silicon atom because of the coupling with the phosphorus nucleus and of analogous values in other hydrido-silyl complexes of the type $Cp'(CO)(PR_3)Mn(H)SiR'_3$ [11]. The Si-H coupling constant of the coordinated silyl group could not be resolved. The singlet in the $^{29}Si\{^1H\}$ NMR spectrum was assigned to the silicon atom of the uncoordinated HMe_2Si-group. In the ^1H NMR spectrum of **2a**, the Si-H couplings of both the coordinated and the uncoordinated groups were not resolved. There are two ^1H NMR and ^{13}C NMR signals for the topologically inequivalent methyl groups at the metal bonded silicon atom. Even for the remote methyl groups of the second, uncoordinated silyl group two separate signals were observed. This effect could be due to the hindered rotation of the bulky aryl group.

The PMnH coupling constant of 59.8 Hz is in the typical range for complexes with a relative *cis* position of the phosphane and the hydride ligands. This corresponds to the geometry of the known complexes of the type $Cp(CO)(PR_3)Mn(H)SiR'_3$ where the small hydride ligand is located between the silyl and the phosphane ligand [11], unless the two groups are forced into a *cis*-position using phosphinoalkylsilanes [13].

All attempts to get the cyclic *bis*(silyl) complex by hydrogen elimination were unsuccessful. Since this could be due to the rigidity of the Mn-Si-C-C-Si-H arrangement in **1a** and **2a**, which could be sterically unfavourable for the transition state, we extended this study to the more flexible 1,2-*bis*(dimethylsilyl) ethane. $Cp'Mn(CO)_2PMe_3$ was employed to compensate the loss of stability in the hydrido silyl complex $Cp'(CO)(PR_3)Mn(H)SiR'_3$ upon changing $SiMe_2$(aryl) to $SiMe_2$(alkyl). When a solution of $Cp'Mn(CO)_2PMe_3$ and an excess of $HMe_2SiCH_2CH_2SiMe_2H$ in petroleum ether was irradiated at −10°C, a violent gas formation was observed. As in the reaction with 1,2-*bis*(dimethylsilyl)benzene, products originating from both the reaction of $Cp'Mn(CO)_3$ (IR bands at 1984 and 1923 cm^{-1}) and $Cp'Mn(CO)_2PMe_3$ (1875 cm^{-1}) with 1,2-*bis*(dimethylsilyl) ethane were observed. Complete separation of all products was not possible by chromatography on silica, and most of the $Cp'Mn(CO)_2(H)SiR_3$ derivatives decomposed. However, a fraction was obtained which only contained products **3a** and **3b** together with some unreacted $Cp'Mn(CO)_2PMe_3$. The ^1H NMR spectrum of this fraction showed two new MeC_5H_4 signals, one new $SiMe_2H$ signal, and two doublets of MnH-groups ($\delta = -12.7$ and −12.9 ppm). In the $^{31}P\{^1H\}$ NMR spectrum, only one new signal was found at 51.5 ppm, and two signals in the $^{29}Si\{^1H\}$ NMR spectrum: a doublet at 33.7 ppm ($^2J_{PMnSi} = 7.3$ Hz), which is assigned to the manganese bonded silicon atom, and a singlet at −10.2 ppm, due to a non-coordinated silicon atom. The two products are obviously very similar; therefore, their ^{31}P- and ^{29}Si NMR signals coincide.

From the chromatographic fraction a yellow powder precipitated after 5 d at −78°C. This compound was spectroscopically identified as the binuclear complex

3b which can even be handled in air for a short time. In the ^{1}H NMR spectrum, the broad doublet at -12.7 ppm with $^{2}J_{PMnH} = 61.4$ Hz was assigned to a Mn-H atom *cis* to the PMe_3 ligand. The absence of a signal for a HMe_2Si group supports the assignment that the precipitated product is the binuclear complex **3b**. Therefore, the second compound in the chromatographic fraction must be the mononuclear complex **3a**.

Since the addition of the second Si-H bond is obviously favoured by electronegative substituents at silicon, we also used 1,1,3,3-tetramethyldisiloxane. Its photochemical reaction with $Cp'Mn(CO)_2PMe_3$ resulted in analogous CO bands in the IR spectrum similar to the reactions with 1,2-*bis*(dimethylsilyl)benzene and 1,2-*bis*(dimethylsilyl)ethane. Column chromatography resulted in the separation of $Cp'Mn(CO)_3$, its very unstable reaction product with the siloxane, and $Cp'Mn(CO)(PMe_3)_2$ from the reaction mixture. One fraction was obtained which contained $Cp'Mn(CO)_2PMe_3$ and the product with the IR band at 1875 cm^{-1}. A broad doublet at -12.7 ppm with $^{2}J_{PMnH} = 64.7$ Hz was obtained in the hydride range of the ^{1}H NMR spectrum. A signal at 5.28 ppm was assigned to a Si-H group. All other signals were in the usual range. The spectroscopic data were consistent with the formation of the mononuclear complex **4a** in analogy to **2a** and **3a**. However, some much weaker additional peaks in the Me*Cp*, PMe_3, and $MnSiMe_2$ range indicated the formation of a small amount of the dinuclear complex **4b**. No extra Mn-H signal was observed which, however, might be too weak or coincide with the signal of **4a**. In the ^{31}P NMR spectrum, two signals at 51.7 and 50.9 ppm were observed, but only one set of signals in the ^{29}Si NMR spectrum (a doublet at 52.4 ppm for MnSi and a singlet at -19.5 ppm for the HMe_2Si group).

Conclusions

The photochemical reaction of $Cp'Mn(CO)_2L$ (L = CO, PMe_3) with the *bis*(silyl) compounds HMe_2Si-X-$SiMe_2H$ ($X = 1,2\text{-}C_6H_4$, C_2H_4, O) results in the formation of the oxidative addition products $Cp'(CO)(L)Mn(H)SiMe_2$-X-$SiMe_2H$ (Eq. (1)). In most cases, a second metal complex fragment can be added, and the binuclear complexes $[Cp'(CO)(L)Mn(H)SiMe_2]_2X$ are also formed. There is no indication that cyclic *bis*(silyl) complexes are formed by intramolecular hydrogen elimination. This corresponds to our previous results with the shorter-chain silanes $HMe_xPh_{2-x}Si$-$SiMe_xPh_{2-x}H$ [10]. The failure to get the cyclic *bis*(silyl) complexes could have several reasons. The methyl substituted Si-H groups might not be acidic enough and/or the electronic properties of the Mn-H group might be unfavourable. Furthermore, the steric situation at the metal center could be too crowded in a *bis*(silyl) complex, or a *cis*-arrangement of the silyl groups could be unfavourable (all known complexes $CpMn(CO)_2(SiR_3)_2$ are *cis*). The chelate effect is in this case not large enough to overcome these restrictions.

Experimental

All operations were performed in an atmosphere of dry and oxygen free nitrogen using dried and argon saturated solvents. For UV irradiation, water cooled mercury high pressure lamps (TQ 150

(180 W) and TQ 718 (700 W), Heraeus) and Pyrex glassware were used. Instrumentation: IR, Perkin Elmer 283; ^{1}H and ^{13}C NMR: Bruker AC 200; ^{31}P{^{1}H} and ^{29}Si{^{1}H} NMR: Jeol FX 90Q.

Photochemical reaction of Cp′Mn(CO)$_3$ with 1,2-bis(dimethylsilyl)benzene

A solution of 1.10 g (5.0 mmol) of *Cp*′Mn(CO)$_3$ and 1.36 g (7.0 mmol) 1,2-*bis*(dimethylsilyl)benzene in 150 ml of petroleum ether was irradiated at −20°C until the new CO bands at 1980 and 1917 cm^{-1} no longer increased in intensity. The yellow solution was then filtered and concentrated *in vacuo* to 20 ml. A yellow and a brown compound which could not be separated precipitated at −25°C.

^{1}H NMR (C_6D_6): $\delta = 7.50$–7.27 (br, m, C_6H_4), 5.41 (br, s, 1 H, SiMe$_2$*H*), 3.96 (br, s, C_5H_4 (from unreacted or re-formed *Cp*′Mn(CO)$_3$ and product), 1.54 (br, s, *Me*Cp), 0.94 (br, s, MnSi*Me*$_2$), 0.38 (br, s, Si*Me*$_2$H (from unreacted silane and product)), −11.71 (br, s, 0.3H, Mn*H*), −12.32 (br, s, 1 H, MnH) ppm.

Photochemical reaction of Cp′Mn(CO)$_2$PMe$_3$ with 1,2-bis(dimethylsilyl)benzene

A solution of 2.66 g (10.0 mmol) of *Cp*′Mn(CO)$_2$PMe$_3$ and 4.50 g (23.0 mmol) 1,2-*bis*(dimethylsilyl)benzene in 150 ml of petroleum ether was irradiated at 0°C for 12 h. The IR spectrum of the reaction mixture then showed bands at 1932, 1881 (*Cp*′Mn(CO)$_2$PMe$_3$ and product **2a**), 1840 (*Cp*′Mn(CO)(PMe$_3$)$_2$), 2010, 1935 (*Cp*′Mn(CO)$_3$, 1980, and 1917 cm^{-1} (**1a**, **1b**). The yellow solution was then filtered, and the solvent was removed *in vacuo*. The resulting yellow oil was dissolved in 10 ml of petroleum ether. Yellow crystals were formed upon standing at −25°C which were recrystallized twice from 5 ml of pentane.

0.6 g (14%); $C_{20}H_{34}MnOPSi_2$ (433.6); ber.: C 55.54, H 7.92; found: C 55.72, H 8.12; IR (pentane): ν(CO) = 1871 cm^{-1}; ^{1}H NMR (C_6D_6): $\delta = 8.02$, 7.57, 7.26 (br, m, 4H, C_6H_4), 5.43 (br, s, 1H, SiMe$_2$*H*), 4.01, 3.75 (br, m, 4H, Me*Cp*), 1.69 (br, s, 3H, *Me*Cp), 1.27, 1.03 (br, s, 6H, MnSi*Me*$_2$), 1.11 (br, d, 9H, P*Me*$_3$, $^{2}J_{PH} = 8.7$ Hz), 0.43 (br, s, 6H, Si*Me*$_2$H), −11.71 (br, d, 1H, Mn*H*, $J_{PMnH} = 59.8$ Hz)ppm; ^{31}P NMR (C_6D_6): $\delta = 52.1$ ppm; ^{29}Si NMR (C_6D_6): 26.1 (d, MnSi, $^{2}J_{PMnSi} = 7.32$ Hz), −24.2 (s, *Si*Me$_2$H)ppm; ^{13}C NMR (C_6D_6: 156.4 (s, C_{aryl}SiMn), 143.1 (s, C_{aryl}SiH), 134.6 (s, 2,5-C_6H_4), 126.9 (s, 3,4-C_6H_4), 97.0 (s, *ipso*-C_5H_4), 85.1, 81.8, 78.1 (C_5H_4), 22.1 (d, PMe, $^{1}J_{PC} = 27.7$ Hz), 13.5 (s, C_5H_4*Me*), 10.7, 8.9 (s, MnSi*Me*), −1.76, −1.92 (s, HSi*Me*)ppm.

Photochemical reaction of Cp′Mn(CO)$_2$PMe$_3$ with 1,2-bis(dimethylsilyl)ethane

A solution of 1.86 g (7.0 mmol) of *Cp*′Mn(CO)$_2$PMe$_3$ and 3.07 g (21.0 mmol) 1,2-*bis*(dimethylsilyl)ethane in 150 ml of petroleum ether was irradiated at −10°C for 5 h. The IR spectrum of the reaction mixture then showed bands at 1932, 1881 (*Cp*′Mn(CO)$_2$PMe$_3$ and products **3a**, **b**), 1984, 1923 (reaction products originating from *Cp*′Mn(CO)$_3$), 2010, 1935 (*Cp*′Mn(CO)$_3$), and 1840 (*Cp*′Mn(CO)(PMe$_3$)$_2$) cm^{-1}. The yellow solution was then filtered, and the solvent was removed *in vacuo*. The resulting yellow oil was dissolved in 3 ml of petroleum ether and chromatographed on silica at −25 °C. Five ill separated fractions were eluted with petroleum ether. Then another fraction was eluted with toluene containing **3a, 3b**, and some *Cp*′Mn(CO)PMe$_3$.When the toluene fraction was concentrated *in vacuo* to 3 ml and kept at −78°C, the dinuclear complex **3b** precipitated as a yellow powder after 5 d.

3b: 100 mg (4.9%); m.p.: 130°C (dec); IR (pentane): ν(CO) = 1867 (s), 1857 (sh) cm^{-1}; ^{1}H NMR (C_6D_6): $\delta = 4.21$ −4.08 (br, m, 4 H, Me*Cp*), 2.02 (br, s, 3 H, *Me*; Cp), 1.17 (br, s, 9 H, PMe), 0.93, 0.80 (br, s, 8 H, CH$_2$, MnSiMe), −12.70 (br, d, 1 H, MnH, $^{2}J_{PMnH} = 61.4$ Hz)ppm; ^{13}C NMR (C_6D_6): $\delta = 96.29$, 84.00, 81.31, 81,10, 78.53 (s, C_5H_4), 23.26 (PMe, $^{1}J_{PC} = 26.5$ Hz), 21.10 (s, CH$_2$), 14.02 (s, Cp-*Me*), 8.09, 6.84 (s, SiMe) ppm; MS (70 eV): *m*/*z* = 297 (*Cp*′(PMe$_3$)Mn(H)SiMe$_2$(CH$_2$)$_2$, 0.1%), 210 (*Cp*′(PMe$_3$)Mn, 16.0%), 196 (*Cp*′(PMe$_2$)Mn, 0.9%), 146 ((HSiMe$_2$CH$_2$)$_2$, 0.5%), 134 (*Cp*′Mn, 9.0%), 87 (HSiMe$_2$(CH$_2$)$_2$, 1.0%, 79(*Cp*′, 4.8%), 76 (PMe$_3$, 2.4%), 59 (HSiMe$_2$, 7.6%).

Photochemical reaction of Cp′Mn(CO)$_2$PMe$_3$ with 1,1,3,3-tetramethyldisiloxane

A solution of 1.86 g (7.0 mmol) of *Cp*′Mn(CO)$_2$PMe$_3$and 2.82 g (21.0 mmol) 1,1,3,3-tetramethyldisiloxane in 150 ml of petroleum ether was irradiated at −10°C for 7 h. The IR spectrum of the reaction mixture then showed bands at 1932, 1881 (*Cp*′Mn(CO)$_2$PMe$_3$ and **4a**, **b**), 1975, 1908 (reaction products originating from *Cp*′Mn(CO)$_3$), 2010, 1935 (*Cp*′Mn(CO)$_3$, and 1840 (*Cp*′Mn(CO)(PMe$_3$)$_2$) cm^{-1}. The yellow solution was concentrated *in vacuo* to 10 ml and chromatographed on silica. The zone containing the products was concentrated. Upon storing at −25°C, part of *Cp*′Mn(CO)$_2$PMe$_3$ precipitated and was separated.

IR (Pentane): ν(CO) = 1875 cm^{-1}; ^{1}H NMR (C$_6$D$_6$): $\delta = 5.28$ (br, s, 1 H, SiH), 4.05 (br, s, 4 H, *Me*Cp), 1.89 (br, s, 3 H, Me*Cp*), 1.24 − 0.86 (br, m, 15 H, PMe$_3$, MnSiMe$_2$), 0.42 (br, s, 6 H, Si*Me$_2$*H) −12.7 (br, d, 1 H, MnH,$^2J_{\mathrm{PMnH}} = 64.7$ Hz) ppm; ^{31}P NMR (C$_6$D$_6$): $\delta = 51.5$, 50.6 (br) ppm;^{29}Si NMR (C$_6$D$_6$): $\delta =$ 52.4 (d, MnSMe$_2$, $^2J_{\mathrm{PMnSi}} = 8.03$), −19.5 (s, SiMe$_2$H)ppm.

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