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Transition metal silyl complexes
Part 54 [1]. Hydrido disilanyl complexes $L_nM(H)SiR_2SiR_2H$ ($L_nM = MeCp(CO)_2Mn$, $Cp(CO)_2Re$, $(CO)_3(PPh_3)Fe$)

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Abstract

Hydrido disilanyl complexes of the type $L_nM(H)SiPh_2SiPh_2H$ are obtained from $HPh_2Si–SiPh_2H$ by photochemical reaction with $MeCp(CO)_3$ or by ligand exchange reactions starting from $MeCpMn(CO)_2(THF)$, $Cp(CO)_2Re(THF)$ or $(CO)_3(PPh_3)Fe(H)SiMe_3$. The dinuclear complex $[MeCp(CO)_2Mn(H)SiPh_2]_2$ is additionally obtained in the photochemical reaction of a 2:1 mixture of $MeCpMn(CO)_3$ and $HSiPh_2SiPh_2H$. When $HMePhSi–SiMePhH$ or $HMe_2Si–SiMe_2H$ is used instead of $HPh_2Si–SiPh_2H$, the kind of products depends on the metal fragment. Both types of complexes are formed when $HMePhSi–SiMePhH$ is reacted with $MeCpMn(CO)_2(THF)$, but only the mononuclear complex is obtained from $CpRe(CO)_2(THF)$ or from $(CO)_3(PPh_3)Fe(H)SiMe_3$. Photochemical reaction of $HMe_2Si–SiMe_2H$ with $MeCpMn(CO)_3$ yields only the dinuclear complex. The outcome of the reaction of $Cp(CO)_2Re(THF)$ with $HMe_2Si–SiMe_2H$ depends on the reaction temperature. At 25°C only *cis*-$Cp(CO)_2Re(H)SiMe_2SiMe_2H$ was spectroscopically observed in low concentration. In refluxing THF, *cis*- and *trans*-$Cp(CO)_2Re(H)SiMe_2SiMe_2H$, and $[Cp(CO)_2Re(H)SiMe_2]_2$ are formed. Reaction of $(CO)_3(PPh_3)Fe(H)SiMe_3$ with $HMe_2Si–SiMe_2H$ gives both $(CO)_3(Ph_3P)Fe(H)SiMeSiMe_2H$ and $[(CO)_3(Ph_3P)Fe(H)SiMe_2]_2$. Photochemical reaction of $Fe(CO)_4PPh_3$ with $HMe_2Si–SiMe_2H$ results in the formation of $(CO)_2(PPh_3)_2Fe(H)_2$. The hydride-bridged complex $[Cp(CO)_2Re]_2(\mu\text{-}H)_2$ is formed as a by-product in the reactions of disilanes with $CpRe(CO)_2(THF)$. Thermal or photochemical decomposition of the complexes $L_nM(H)SiPh_2SiPh_2H$ preferentially proceeds by reductive elimination of the disilane. Only in the decomposition of $MeCp(CO)_2Mn(H)SiPh_2SiPh_2H$ some H_2 is observed, which may be due to a 1,2-H_2 elimination.

Keywords: Disilanyl complexes; Hydride complexes; Disilanes; Photochemical reactions; Reductive elimination

1. Introduction

There are numerous examples for the formation of stable hydrido silyl complexes $L_nM(H)SiR_3$ by oxidative addition of hydrogenosilanes to coordinatively unsaturated metal complexes (L_nM), with a great variation of L_nM and the groups R at silicon. However, only very few hydrido disilanyl complexes $L_nM(H)SiR_2SiR_3$ have been prepared. Disilanyl complexes $L_nMSiR_2SiR_3$ *without* an additional hydride ligand have been well investigated and exhibit an interesting rearrangement chemistry. This topic was recently reviewed elsewhere [2].

The objective of this work was to prepare hydrido disilanyl complexes with a β-SiH group. The question behind was whether disilene complexes $L_nM(\eta^2\text{-}SiR_2{=}SiR_2)$ can be obtained from the complexes $L_nM(H)SiR_2SiR_2H$ by intramolecular 1,2-hydrogen elimination. There are two possible pathways for a H_2 elimination: the first is oxidative addition of the β-SiH group to the metal centre after elimination of one of the co-ligands L. This process might be favoured by subsequent elimination of H_2, with the option of a recoordination of L. The other possiblity is the formation of bis(silyl) complexes $L_nM(SiR_3)_2$ without the intermediate generation of unsaturated complexes. There are several examples for saturated hydrido silyl complexes $L_nM(H)SiR_3$ reacting with $HSiR_3$ by H_2 elimination (for example, see Ref. [3]). The mechanism of these reactions is unknown in most cases, but probably proceeds via a four-centre transition state. Although the substituents at silicon appear to have a great influence on the formation of bis(silyl) complexes by this route, the 'ring closure' of $L_nM(H)SiR_2SiR_2H$ by H_2 elimination might be favoured by entropy.

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[1] Part 53, see Ref. [1].

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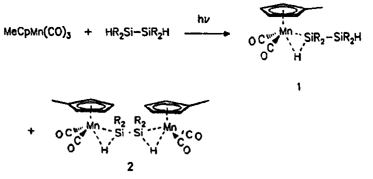
Hydrido silyl derivatives of metal carbonyl complexes are usually prepared by UV irradiation of the parent metal carbonyl in the presence of the silane in an inert solvent. The silane is oxidatively added after photochemical generation of the unsaturated metal complex. However, most of the known disilanyl derivatives of metal carbonyls (and the disilanes themselves) exhibit a rich photochemistry. For this reason, preparative problems were anticipated for the photochemical reaction of disilanes with metal carbonyls. We therefore looked for alternative routes to prepare the hydrido disilanyl complexes, particularly by substitution of labile ligands.

2. Results and discussion

Many hydrido silyl complexes of the type $(C_5R'_5)(CO)_{2-x}L_xMn(H)SiR_3$ have already been prepared, with a variety of silyl groups, and ligands L and $C_5R'_5$ [4–6]. The silyl group and the hydride ligand are always *cis*. This is probably due to the Mn,H,Si three-centre two-electron bonding situation observed in most of these complexes. Complexes of this type are only stable towards reductive elimination of the silane, if either the silyl group (sufficiently electronegative substituents R) or the metal fragment (small and/or electron-donating ligands) provide sufficient stabilization.

The hydrido silyl complexes $(C_5R'_5)(CO)_{2-x}L_xMn(H)SiR_3$ are usually prepared by the photochemical route. The dinuclear complex $[(C_5Me_5)(CO)_2Mn(H)]_2SiH_2$ was prepared by reaction of $MeCpMn(CO)_2(THF)$ with SiH_4 [7]. However, reaction of the THF complex with $HSiR_2Cl$ gave the hydrido silyl complexes only as byproducts. The main product was the siloxycarbyne complexes $[MeCp(CO)Mn(\mu\text{-}COSiR_2H)]_2$ [8].

When a petroleum ether solution of $MeCp(CO)_3$ was irradiated in the presence of one equivalent of $HPh_2Si–SiPh_2H$, the hydrido disilanyl complex **1a** was obtained in low yields (Eq. (1)). The spectroscopic data, particularly the ^{29}Si NMR spectra (two signals at −27.37 and −2.62 ppm for the uncoordinated and coordinated Si atoms) and the SiH signal in the ^1H NMR spectrum, clearly showed that a complex of the type $L_nM(H)SiR_2SiR_2H$ was formed.



$SiR_2 = SiPh_2$:	**1a**	–
$SiR_2 = SiPhMe$:	–	**2b**
$SiR_2 = SiMe_2$:	–	**2c**

When HMePhSi–SiMePhH (mixture of diastereomers) or $HMe_2Si–SiMe_2H$ was used instead of $HPh_2Si–SiPh_2H$, only the binuclear complexes **2b,c** with a bridging Si_2R_4 unit were formed, even with an excess of the disilane. The tetramethyl derivative **2c** slowly decomposed at room temperature and was therefore only spectroscopically characterized. The instability of **2c** is not unexpected, since $Cp(CO)_2Mn(H)Si(alkyl)_3$ derivatives are least electronically stabilized and therefore readily decompose by reductive elimination of the silane. For example, *cis*-$Cp(CO)_2Mn(H)SiEt_3$ was spectroscopically observed at 25°C in the presence of excess $HSiEt_3$, but decomposed as soon as the silane was removed [6].

While the Si_2R_2-bridged dinuclear complexes **2** were exclusively formed for $SiR_2 = SiMe_2$ or SiPhMe and no mononuclear complexes $MeCp(CO)_2Mn(H)SiR_2SiR_2H$ were observed, both types of complexes were obtained for $SiR_2 = SiPh_2$, when a 2:1 mixture of $MeCpMn(CO)_3$ and $HSiPh_2SiPh_2H$ was employed (Eq. (2)).

$$2MeCpMn(CO)_3 + HPh_2Si–SiPh_2H \rightarrow \mathbf{1a} + \underset{\mathbf{2a}}{[MeCp(CO)_2Mn(H)SiPh_2]_2} \quad (2)$$

The spectra of **2a–c** are distinctly different to those of **1a** and show the silicon atoms being chemically equivalent. The complex **2b** was obtained as a mixture of diastereomers, because the disilane was employed as a mixture of diastereomers. The expected two sets of NMR signals were only observed in the ^{29}Si NMR spectrum, and for the CO ligands in the ^{13}C NMR spectrum. The other signals of the two diastereomers in the ^1H and ^{13}C NMR spectra were not resolved (as in the parent disilane).

The *cis* arrangement of the two CO ligands in **1** and **2**, and thus the *cis* arrangement of H and Si, is concluded from the relative intensity of the $\nu(CO)$ vibrations. The same geometry was found in all known $Cp(CO)_2Mn(H)SiR_3$ derivatives. The Mn,H,Si coupling constants were determined for **1a** (57 Hz) and **2b** (61 Hz). Their magnitude clearly shows that the complexes **1** and **2** contain three-centre-two electron bonds [9], as expected.

Oxidative addition of an Si–H bond to transition metal centres is, inter alia, promoted by electron-withdrawing substituents at silicon. Thus, the oxidative addition of the first Si–H bond of $HR_2Si–SiR_2H$ is more favourable for R = Ph than for R = Me. Oxidative addition of the β-SiH group in the thus formed complexes $L_nM(H)SiR_2SiR_2H$ to a second metal complex fragment should be more favourable than addition of the first SiH group, because the hydride substituent is replaced by the more electron-withdrawing L_nM 'substituent'. In the light of these electronic arguments it is surprising that formation of **2a** from **1a** obviously is less favourable than in the $SiMe_2$ and SiMePh derivatives. The only explanation is that addition of the second MeCp(CO)$_2$Mn fragment is inhibited by the bulkier phenyl groups.

To check whether the preferred formation of **1** or **2** is influenced by photochemical processes, we also reacted the solvent complexes $MeCpMn(CO)_2(THF)$ and $MeCpMn(CO)_2(OEt_2)$ with the disilanes. Upon reaction of $MeCpMn(CO)_2(THF)$ with $HPh_2Si–SiPh_2H$ only the mononuclear complex **1a** was formed (Eq. 3), as in the photochemical reaction, but the yield (15%) was higher. The time required to complete the reaction (14 h) can be shortened to 1 h by using $MeCpMn(CO)_2(OEt_2)$ instead of the THF complex.

$$MeCpMn(CO)_2(THF) + HR_2Si–SiR_2H \rightarrow \mathbf{1} + \mathbf{2} \qquad (3)$$

$SiR_2 = SiPh_2$:	**1a**	–
$SiR_2 = SiPhMe$:	**1b**	**2b**

Reaction of $MeCpMn(CO)_2(THF)$ with HMePhSi–SiMePhH resulted in the formation of two hydride complexes. By comparison of the NMR spectra, one of them was identified as the Si_2R_4-bridged complex **2b**, already obtained by the photochemical route. Although the second complex was not isolated, due to decomposition during work-up, the ^1H NMR spectrum showed the typical signals of the mononuclear complex **1b**, particular a SiH signal at 4.8 ppm.

Complex **1a** has a suitable substitution pattern for the desired 1,2-H_2 elimination. The previously described lower yield in the photochemical preparation route indicated some photochemical decomposition pathway. We therefore irradiated a petroleum ether solution of **1a** at −20°C until the IR spectrum indicated the complete destruction of the complex. The evolved gas was collected and analysed by gas chromatography. A peak of H_2 was detected. The ^{29}Si NMR spectrum of the reaction solution showed a strong signal at −34.50 ppm and a weaker signal at −17.53 ppm. The former signal is characteristic for the disilane $HPh_2Si–SiPh_2H$, while the latter can possibly be attributed to $HSiPh_3$.

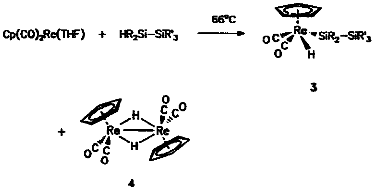
The main decomposition reaction is obviously the reductive elimination of the disilane. The formation of $HSiPh_3$ indicates some additional rearrangement reaction, possibly similar to those extensively investigated for $CpFe(CO)_2SiR_2SiR_3$ complexes [2]. However, the formation of H_2 points to a third reaction, which could be the anticipated 1,2-H_2 elimination. Polysilanes, which would be formed by decomposition products of an intermediate η^2-$Ph_2Si{=}SiPh_2$ complex, were not detected. They may be contained in the unsoluble byproducts, which we did not analyse.

To check whether the formation of hydrogen is associated with the presence of the β-SiH group, we also prepared *cis*-$MeCp(CO)_2Mn(H)SiPh_2SiMe_3$ for comparison from $MeCpMn(CO)_2(OEt_2)$ and $HPh_2Si–SiMe_3$ according to Eq. (3). There was no formation of hydrogen upon photochemical decomposition, and the only soluble silicon compound in the reaction solution was $HPh_2Si–SiMe_3$. The absence of H_2 among the decomposition products of $MeCp(CO)_2Mn(H)SiPh_2SiMe_3$ is an indication that at least a minor decomposition route of **1a** involves the β-SiH group. However, the dominant decomposition pathway in every case is the reductive elimination of the disilane.

We therefore tried to prepare hydrido disilanyl complexes of the type $L_nM(H)SiR_2SiR_2H$ with metal fragments which are less prone to reductive elimination reactions. It is known from the work of Graham et al. [10] that the stability of hydrido silyl complexes of rhenium, $Cp(CO)_2Re(H)SiR_3$ towards reductive elimination is markedly higher than that of the corresponding manganese complexes. The complexes have been prepared by the photochemical route from $CpRe(CO)_3$. Both the *cis* and the *trans* isomers were observed, depending on the silane [10,11]. The reactions are complicated by the fact that complete conversion of $CpRe(CO)_3$ without decomposition of the product is not possible and that separation of the complexes is difficult. The dihydride complex *trans*-$Cp(CO)_2Re(H)_2$ was formed upon chromatography of $Cp(CO)_2Re(H)SiHEt_2$ on silica [11].

The preparation of the manganese complexes **1** and **2** had shown that exchange of a labile ligand results in higher yields than the photochemical route, probably because of the photolability of the products. We therefore reacted the disilanes with the solvent complex $Cp(CO)_2Re(THF)$. Irradiation of $CpRe(CO)_3$ in THF in a quartz vessel results in a 50% conversion of the tricarbonyl [12]. When $HPh_2Si–SiPh_2H$ was reacted with this solution in refluxing THF, the formation of two complexes was observed (Eq. (4)). One of them was identified as the desired disilanyl complex **3a** and the other as $[Cp(CO)_2Re]_2(\mu\text{-}H)_2$ (**4**). NMR spectra of the reaction solution showed that **4** is already formed during the reaction and not during work-up.

In contrast with the manganese system, reaction of HMePhSi–SiPhMeH with $Cp(CO)_2Re(THF)$ yielded the mononuclear complex **3b**.



(4)

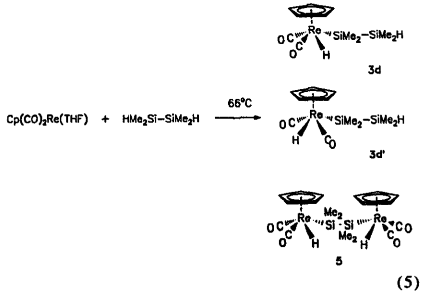
3a: $SiR_2SiR'_3 = SiPh_2SiPh_2H$
3b: $SiR_2SiR'_3 = SiMePhSiMePhH$
3c: $SiR_2SiR'_3 = SiPh_2SiMe_3$

The complexes **3** have a *cis* arrangement of the hydride and the disilanyl ligand, according to the relative intensity of the $\nu(CO)$ bands. The NMR spectra clearly exclude the formation of Si_2R_4-bridged complexes. Complex **3b** was formed as a mixture of diastereomers, which give rise to two sets of NMR signals. An unequivocal assignment was possible from the signal intensities, because one diastereomer was formed in a slight excess (10:9 ratio). The hydride complex was identified by comparison with the spectroscopic data of the known complex $[(C_5Me_5)(CO_2)Re]_2(\mu\text{-}H)_2$ [13], which are very similar.

$[(C_5Me_5)(CO)_2Re]_2(\mu\text{-}H)_2$ was obtained by reaction of H_2 with $(C_5Me_5)_2Re_2(CO)_4$, which is a decomposition product of $(C_5Me_5)(CO)_2Re(THF)$. To check whether **4** is formed in the same way, with H_2 possibly originating from the decomposition of **3a,b**, we also reacted $HPh_2Si\text{–}SiMe_3$ with $Cp(CO)_2Re(THF)$ under the same conditions. Despite the absence of a β-hydrogen atom, the hydride complex **4** was formed, together with the disilanyl complex **3c**. The hydride complex **4** was not formed when a THF solution of $Cp(CO)_2Re(THF)$ was heated without a silane. We currently do not know the role of the disilane in the formation of **4**. However, the control experiment with $HPh_2Si\text{–}SiMe_3$ showed that 1,2-elimination of H_2 from **3a,b** cannot be the source for the hydride ligands in **4**.

The outcome of the reaction of $Cp(CO)_2Re(THF)$ with $HMe_2Si\text{–}SiMe_2H$ depended on the reaction temperature. At 25°C only *cis*-$Cp(CO)_2Re(H)SiMe_2SiMe_2H$ (**3d**) was spectroscopically observed in low concentration. The *cis* geometry was concluded from the IR spectrum. The NMR data, particularly the SiH signal, split to a septet by the two methyl groups, clearly proved that only one $Cp(CO)_2Re$ moiety was oxidatively added. In refluxing THF, **3d** is the major product (Eq. (5)). However, two other hydride complexes were additionally observed, none of them being **4**. We were not able to separate the products, but the spectra allowed to determine their constitution.

One byproduct has a set of NMR signals very similar to that of **3d**. We therefore assign these signals to the *trans* isomer **3d'**. This is not surprising, because the photochemical synthesis of $Cp(CO)_2Re(H)Si(CH_2Ph)_3$, the only well-characterized hydrido silyl complex of rhenium without aryl substituents, also lead to a mixture of the *cis* and *trans* isomer [10]. The second byproduct is the Si_2Me_2-bridged dinuclear complex **5**. This assignment is mainly based on the absence of a SiH signal and the appearance of only one SiMe resonance.

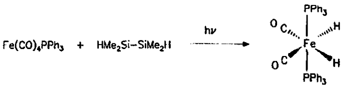


(5)

We selected **3a** for decomposition experiments. The compound turned out to be thermally very robust. Refluxing a solution of **3a** in toluene or CH_2Cl_2 for several hours did not result in any noticable decomposition. However, irradiation of a C_6D_6 solution led to complete decomposition within 1 h. The ^{29}Si NMR spectrum of the solution showed only one signal at −34.06, assigned to uncoordinated $HPh_2Si\text{–}SiPh_2H$. The conclusion from this experiment corroborates the results from the corresponding manganese complex: reductive elimination of the silane is the preferred decomposition pathway, even with a metal fragment less prone to reductive elimination reactions.

We checked this point with complexes of the type $(CO)_3(PR_3)Fe(H)SiR_3$ also known to be rather insensitive towards reductive elimination of the silane. Their best way of preparation is the photochemical route, starting from $Fe(CO)_4PR_3$ [4,14,15]. There is complete oxidative addition of the silane, with H and SiR_3 being *cis*. Most of the known complexes $(CO)_3(PR_3)Fe(H)SiR_3$ have a *meridional* geometry. They can also be prepared by CO–PR_3 exchange from $(CO)_4Fe(H)SiR_3$ [14,16]. However, this method is not very general, one of the complications being deprotonation by basic phosphanes [14].

Photochemical reaction of $Fe(CO)_4PPh_3$ with $HMe_2Si\text{–}SiMe_2H$ in petroleum ether at 0°C did not result in the formation of $(CO)_3(PPh_3)Fe(H)SiMe_2SiMe_2H$, but instead the dihydride complex **6** was formed (Eq. (6)). The complex is insoluble in petroleum ether and ether, slightly soluble in toluene and well soluble in chlorinated hydrocarbons. Solutions of **6** slowly decompose.



6

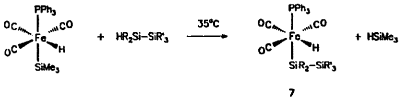
(6)

The dihydride complex **6** was previously obtained by reaction of $[Fe(p\text{-}N_2C_6H_4F)(CO)_2(PPh_3)_2]BF_4$ with $NaBH_4$, but only characterized by IR spectroscopy [17]. However, the NMR data are similar to the related complexes $(CO)_2(PR_3)_2Fe(H)_2$ ($PR_3 = P^nBu_3$, PMe_2Ph), prepared by reaction of $K[(CO)_4Fe(H)]$ with PR_3 [18]. The triplets in the ^1H (−9.24 ppm) and ^{31}P NMR spectrum (81.36 ppm) show the existence of two chemically equivalent hydride and PPh_3 ligands. The coupling constant of 58.6 Hz is very similar to that in the P^nBu_3 and PMe_2Ph complex.

The formation of dihydride complexes was previously observed in other reactions of silanes with iron carbonyl derivatives. Reaction of $(CO)_4Fe(H)SiR_3$ ($SiR_3 = SiPh_3$, $SiMe_2Ph$) with dppe resulted in the formation of $(CO)_2(dppe)Fe(H)_2$, and the reaction of $(CO)_2[P(OPh)_3]_2Fe(H)SiMe_2Ph$ with $HSiMe_2Ph$ gave $(CO)_2[P(OPh)_3]_2Fe(H)_2$ [19]. The mechanism of these reactions is not known, as in the present case.

Because the photochemical route did not give the desired complexes, we chose a thermal route. There are several examples for the exchange of silanes in hydrido silyl complexes [20]. Particularly useful are the $SiMe_3$ derivatives, because $HSiMe_3$ is volatile. This allows the shifting of the exchange equilibrium. The complex $(CO)_3(PPh_3)Fe(H)SiMe_3$ is photochemically obtained from $Fe(CO)_4PPh_3$ and $HSiMe_3$. Elimination of $HSiMe_3$ from this complex was already utilized for the preparation of the hydrido stannyl complexes $(CO)_3(PPh_3)Fe(H)SnR_3$ [21].

Reaction of *mer*-$(CO)_3(PPh_3)Fe(H)SiMe_3$ with $HPh_2Si–SiPh_2H$, HMePhSi–SiMePhH or $HPh_2Si–SiMe_3$ (the latter was again reacted for comparison) resulted in the clean formation of the hydrido disilanyl complexes **7** (Eq. (7)). There was no indication for the formation of the corresponding Si_2R_4-bridged complexes, even when **7a** was treated with an excess of $(CO)_3(PPh_3)Fe(H)SiMe_3$. This is probably again due to steric reasons.



(7)

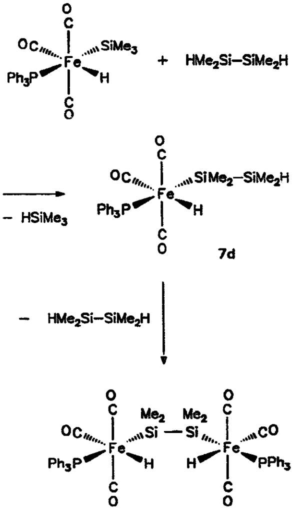
7a: $SiR_2SiR'_3 = SiPh_2SiPh_2H$
7b: $SiR_2SiR'_3 = SiMePhSiMePhH$
7c: $SiR_2SiR'_3 = SiPh_2SiMe_3$

The NMR spectra show again the typical features of the mononuclear complexes. An additional feature is the PFeSi coupling of the metal-bound silicon atom. The $PFeC_{CO}$ and PFeH coupling constants compare well to the known complexes of the type *mer*-$(CO)_3(PPh_3)Fe(H)SiR_3$. For **7b** the two diastereomers give two well separated sets of NMR signals.

The reaction of $(CO)_3(PPh_3)Fe(H)SiMe_3$ with $HMe_2Si–SiMe_2H$ took again a different course. When the reaction was carried out in a toluene solution at 25°C, the formation of **7d** was first observed (monitored by ^{31}P NMR spectroscopy). Another hydride complex was formed in a much slower reaction, identified as the Si_2Me_2-bridged complex **8** (Eq. (8)). Formation of **8** already starts, when unreacted $(CO)_3(PPh_3)Fe(H)SiMe_3$ is still present. For example, the $(CO)_3(PPh_3)Fe(H)SiMe_3$:**7d**:**8** ratio after 26 h was 1:6:2. The conversion of **7d** to **8** is complete after 5 days.

The complex **8** was identified by the typical NMR features discussed earlier. Contrary to the other iron complexes, no SiFeP coupling was observed.

A resonable explanation for the formation of **8** would be that reductive elimination of $HMe_2Si–SiMe_2H$ from **7d** is rather easy (due to the electon-donating methyl groups). The thus formed unsaturated $(CO)_3(PPh_3)Fe$ then reacts with **7d** to give **8**.



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(8)

The formation of related Si_2R_2-bridged complexes from **7a,b** was not observed, even when solutions of these complexes were heated to 50°C. Only $Fe(CO)_3(PPh_3)_2$ and $Fe(CO)_4PPh_3$ were formed. These metal carbonyl derivatives are typically formed during reductive elimination. The same decomposition behaviour was found for **7c**, the presence of the *β*-SiH group has again no influence on the decomposition pathway.

3. Conclusions

Two types of complexes are formed in the reaction of disilanes $HR_2Si–SiR_2H$ with coordinatively unsaturated metal complex fragments (L_nM): the mononuclear compounds $L_nM(H)SiR_2SiR_2H$ and the dinuclear compounds $L_nM(H)SiR_2SiR_2(H)ML_n$. Formation of the latter compounds appears to be favoured for electronic reasons, because the electron-withdrawing L_nM fragment in $L_nM(H)SiR_2SiR_2H$ activates the second SiH group towards oxidative addition. The dinuclear compounds are exclusively formed when $HMe_2Si–SiMe_2H$ is employed. With the disilanes HMePhSi–SiMePhH and $HPh_2Si–SiPh_2H$ both types of complexes are observed, depending on the kind of metal complex fragment and, in the case of $L_nM = MeCp(CO)_2Mn$, of the molar ratio of the starting compounds. In the series $HMe_xPh_{2-x}Si–SiMe_xPh_{2-x}H$ ($x = 1, 2$) the tendency to form the dinuclear complexes $L_nM(H)SiR_2SiR_2(H)ML_n$ decreases with decreasing x. We attribute this to steric effects, which render the approach of the metal fragment to the second SiH group more diffucult.

The decomposition of the complexes $L_nM(H)SiR_2SiR_2H$ is governed by the reductive elimination of the SiH bond, i.e. the presence of the β-SiH group does not change the chemical behaviour of the complexes significantly (compared to the corresponding monosilyl complexes $L_nM(H)SiR_3$). The only indication for a 1,2-elimination of H_2 was found in the photochemical decomposition of the manganese complex **1a**, where minor amounts of H_2 were detected. Our results show that 1,2-elimination of H_2 from complexes of the type $L_nM(H)SiR_2SiR_2H$ obviously is no reasonable alternative to the existing methods to prepare η^2-Si_2R_2 complexes. Future work will be directed towards the question, whether 'backbiting' of a $(SiR_2)_nH$ ligand to form cyclic products is possible for $n > 2$.

4. Experimental

All operations were performed in an atmosphere of dry and oxygen-free argon, using dried and nitrogen-saturated solvents. A high pressure Hg lamp (Heraeus TQ 150, 180 W) was used for the photochemical reactions. Column chromatography was performed with silica (Merck 60, <0.063 mm mesh) as the stationary phase, from which oxygen and water was removed by heating in vacuo and storage under N_2. IR spectra: Perkin-Elmer 283 or 1210, CaF_2 cuvettes. NMR spectra: Bruker AC 200, AC 250, AMX 400, Jeol PMX 60 SI. The spectra were taken at 25°C, if not otherwise stated.

4.1. Photochemical preparation of $MeCp(CO)_2Mn(H)SiPh_2SiPh_2H$ (1a)

430 mg (2.0 mmol) of $MeCpMn(CO)_3$ and 720 mg (2.0 mmol) of HPh_2Si–$SiPh_2H$ were dissolved in 120 ml of petroleum ether and irradiated at −10°C until the intensity of the new IR bands at 1986 and 1927 cm^{-1} no longer increased (about 4 h). The solvent was then removed in vacuo and the obtained brown oil dissolved in 15 ml of CH_2Cl_2. After filtration over silica, the solvent was removed again and the residue chromatographed on silica at −10°C with petroleum ether–Et_2O (10:1). Several fractions were eluted, the one carrying the product was identified by IR spectroscopy. This fraction was concentrated in vacuo until **1a** started to precipitate. Precipitation was completed at −78°C. Yield 98 mg (9%), m.p. 76°C (dec.). IR (Et_2O) ν(SiH) 2105 (w), ν(CO) 1978 (vs), 1921 (s); ^1H NMR (C_6D_6, 400.1 MHz) δ −10.71 (s, 1 H, MnH, J(SiH) 57 Hz), 1.34 (s, 3 H, $C_5H_4CH_3$), 3.89 (s, 4 H, $C_5H_4CH_3$), 5.69 (s, 1 H, SiH, ^1J(SiH) 173 Hz), 6.95–7.78 (m, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz) δ 12.82 ($C_5H_4CH_3$), 83.18, 83.46 (C2 and C3 of $C_5H_4CH_3$), 101.76 (ipso C of $C_5H_4CH_3$), 127.88, 128.12, 129.00, 129.44, 134.86, 136.06, 136.52, 140.77 (C_6H_5), 228.28 (CO); $^{29}Si\{^1H\}$ NMR (C_6D_6, 79.5 MHz) δ −27.37 ($SiPh_2H$), −2.62 ($MnSiPh_2$). *Anal.* Found: C, 68.74; H, 5.33. Calc. for $C_{32}H_{30}MnO_2Si_2$ (557.7): C, 69.04; H, 5.25%.

4.2. Photochemical preparation of $[MeCp(CO)_2Mn(H)SiMeR]_2$ (2b: R = Ph; 2c: R = Me)

1.3 g (6.0 mmol) of $MeCpMn(CO)_3$ and 2.9 g (12.0 mmol) of HMePhSi–SiMePhH mixture of diastereomers) or 1.42 g (12.0 mmol) of HMe_2Si–$SiMe_2H$ in 120 ml of petroleum ether were irradiated at −10°C until the IR spectra showed no further change of the ν(CO) bands (24 h or 11 h). The solution was then filtered at 0°C and the solvent removed in vacuo.

2b: The pale yellow solid was dissolved in 70 ml of toluene and filtered over silica gel. The solvent was removed in vacuo, and the solid washed with pentane. Yield 435 mg (23%), m.p. 88°C (dec.). IR (toluene) ν(CO) 1970 (vs), 1910 (s); ^1H NMR (C_6D_6, 400.1 MHz) δ −11.16 (s, 1 H, MnH, J(SiH) 57 Hz), 1.20 (s, 3 H, $C_5H_4CH_3$), 1.53 (s, 3 H, SiMe), 3.71–3.85 (m, 4 H, $C_5H_4CH_3$), 6.95–7.60 (m, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz) δ 4.07 (SiMe), 13.31 ($C_5H_4CH_3$), 81.79, 82.51 (C2 and C3 of $C_5H_4CH_3$), 100.92 (ipso C of $C_5H_4CH_3$), 134.45 134.61, 134.29, 142.76 (C_6H_5), 229.47, 229.71 (CO); $^{29}Si\{^1H\}$ NMR (C_6D_6, 79.5 MHz) δ −3.57, −2.85. *Anal.* Found: C, 58.05; H, 5.23. Calc. for $C_{30}H_{32}Mn_2O_4Si_2$ (622.6): C, 57.87; H, 5.18%.

2c: The brown–red oil was chromatographed on silica gel with petroleum ether at 0°C. A yellow zone of $MeCpMn(CO)_3$ was eluted first, and then a red zone with toluene. The latter was filtered over silica gel. The red solution quickly got turbid again due to decomposition of the product. A brown–red oil was obtained after removal of the solvent in vacuo. IR (petroleum ether) ν(CO) 1978 (vs), 1915 (s); ^1H NMR (C_6D_6, 400.1 MHz) δ −12.85 (s, 1 H, MnH), 0.24 (s, 6 H, SiMe), 1.43 (s, 3 H, $C_5H_4CH_3$), 3.86 (s, 4 H, $C_5H_4CH_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz) δ 1.38 (SiMe), 13.14 ($C_5H_4CH_3$), 81.94, 82.13 (C2 and C3 of $C_5H_4CH_3$), 102.68 (ipso C of $C_5H_4CH_3$), 225.66 (CO).

4.3. Photochemical reaction of $MeCpMn(CO)_3$ with 0.5 equivalents of HPh_2Si–$SiPh_2H$

1.10 g (6.0 mmol) of $MeCpMn(CO)_3$ and 1.31 g (3.0 mmol) of HPh_2Si–$SiPh_2H$ in 120 ml of petroleum ether were irradiated at −10°C until the IR spectra showed no further change of the ν(CO) bands. The solution was concentrated to 30 ml. A yellow solid was filtered off, dissolved in 20 ml of toluene and filtered. The solvent was removed in vacuo and the yellow oil washed five times at 0°C with 5 ml petroleum ether each. According to the NMR spectra, the yellow solid contained both **1a** and **2a**. ^1H NMR of **2a** (C_6D_6, 200.1 MHz) δ −10.99 (s, MnH), 1.34 (s, 3 H, $C_5H_4CH_3$), 3.66–3.76 (m, 4 H, $C_5H_4CH_3$), 7.1–7.8 (m, 10 H, C_6H_5).

Chromatography of the mixture at −5°C on silica with CH_2Cl_2 only resulted in the recovery of **1a**. The complex **2a** decomposed during chromatography.

4.4. Thermal reaction of $MeCpMn(CO)_2(OR_2)$ (OR_2 = THF or Et_2O) with $HPh_2Si–SiPh_2H$

250 mg (1.2 mmol) of $MeCpMn(CO)_3$ in 120 ml of THF were irradiated at −25°C until the IR spectrum showed the complete formation of $MeCpMn(CO)_2(THF)$. The lamp was switched off, and 660 mg (1.8 mmol) of $HPh_2Si–SiPh_2H$ were added. The solution was warmed to 25°C and stirred for additional 14 h. The solvent was removed in vacuo. The obtained yellow oil was chromatographed at −10°C on silica with petroleum ether–toluene (4:1). After removal of the solvent the yellow oil was recrystallized from 5 ml Et_2O by addition of 10 ml petroleum ether at −78°C. The obtained solid was dried in vacuo. Yield 98 mg (15%).

The same reaction was performed by reaction of the Et_2O complex [500 mg (2.3 mmol) of $MeCpMn(CO)_3$ in 120 ml Et_2O irradiated at −40°C for 3 h; 730 mg (2.0 mmol) of $HPh_2Si–SiPh_2H$]. Reaction with the disilane was complete after 1h. Yield 210 mg (19%).

4.5. Thermal reaction of $MeCpMn(CO)_2(THF)$ with HMePhSi–SiMePhH

$MeCpMn(CO)_2(THF)$ was prepared from 250 mg (1.2 mmol) of $MeCpMn(CO)_3$ in 120 ml THF at −25°C as described above. 472 mg (1.8 mmol) of HMePhSi–SiMePhH (mixture of diastereomers) was then added. The solution was warmed to 25°C and stirred for additional 18 h. Then the solvent was removed in vacuo. The resulting brown oil was dissolved in 30 ml toluene and the solution filtered over Celite. Removal of the solvent in vacuo gave a brown oil, which showed the ^1H NMR signals of **2b** and additional signals assigned to **1b**. ^1H NMR of **1b** (C_6D_6, 400.1 MHz) δ −11.50 (s, MnH), 0.2–1.3 (m), 1.44 (s, $C_5H_4C\mathit{H}_3$), 3.76 (s, $C_5\mathit{H}_4CH_3$), 4.8 (m, SiH).

Chromatography on silica at 0°C with petroleum ether–Et_2O (4:1) resulted in the decomposition of **1b**. The complex **2b** was isolated in 22% yield (79 mg).

4.6. Photochemical decomposition of 1a

36 mg (0.1 mmol) of **1a** in 120 ml of petroleum ether was irradiated at −20°C until the bands of **1a** had disappeared in the IR spectrum (about 2 h). The evolved gas was collected and showed a H_2 signal in the gas chromatogram. The solvent was removed from the solution in vacuo and the solid residue dissolved in C_6D_6 for ^{29}Si NMR spectroscopy (25°C, 79.5 MHz: strong signal at −34.50 ppm and a weak signal at −17.53 ppm).

4.7. Preparation of $MeCp(CO)_2Mn(H)SiPh_2SiMe_3$

The compound was obtained from $MeCp(CO)_2Mn(OEt_2)$ [from 600 mg (2.8 mmol) of $MeCpMn(CO)_3$] and 710 mg (2.8 mmol) of $HPh_2Si–SiMe_3$ as a yellow oil as described above. Yield 368 mg (30%). IR (petroleum ether) ν(CO) 1978 (vs), 1920 (s); ^1H NMR (C_6D_6, 250.1 MHz) δ −11.28 (s, 1 H, J(SiH) = 56 Hz, MnH), 0.32 (s, 9 H, ^1J(SiH) = 120 Hz, $SiMe_3$), 1.48 (s, 3 H, $C_5H_4C\mathit{H}_3$), 3.99–4.03 (m, 4 H, $C_5\mathit{H}_4CH_3$), 7.28–7.78 (m, 10 H, $C_6\mathit{H}_5$); $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz) δ −0.55 ($SiMe_3$), 12.88 ($C_5H_4\mathit{C}H_3$), 82.80, 83.56 (C2 and C3 of $\mathit{C}_5H_4CH_3$), 101.59 (ipso C of $\mathit{C}_5H_4CH_3$), 127.94, 128.61, 135.86, 141.63 (C_6H_5), 229.34 ($\mathit{C}O$); $^{29}Si\{^1H\}$ NMR spectrum (C_6D_6, 49.7 MHz) δ −12.11 ($SiMe_3$), −18.34 (MnSi).

4.8. Reaction of $CpRe(CO)_2(THF)$ with $HPh_2Si–SiPh_2H$, HMePhSi–SiMePhH or $HPh_2Si–SiMe_3$

A solution of 2–3 mmol of $CpRe(CO)_3$ in 120 ml THF was irradiated at 0°C in a quartz vessel, until the intensity ratio of the ν(CO) bands of $CpRe(CO)_3$ and $CpRe(CO)_2(THF)$ no longer changed (1:1 ratio). After addition of $HR_2SiSiR'_3$, the solution was concentrated in vacuo to 30 ml and refluxed for 1 h. The solvent was then removed in vacuo and the resulting brown oil chromatographed at 0°C on silica with petroleum ether–CH_2Cl_2 (7:3) (**3a** and **3c**). Fractions of 10 ml each were collected and analysed by IR spectroscopy. The oil resulting from the reaction of HMePhSi–SiMePhH was first chromatographed at 0°C with petroleum ether–Et_2O (1:1), and the fraction carrying the product again with petroleum ether–Et_2O (10:1). The fractions containing **3** were combined and concentrated in vacuo until precipitation started. Precipitation of **3** was completed at −78°C.

3a: 1.05 g (3.1 mmol) of $CpRe(CO)_3$ and 1.2 g (3.2 mmol) of $HPh_2SiSiPh_2H$. Colourless solid; yield 467 mg (22%), m.p. 79°C (dec.). IR (Et_2O) ν(CO) 1990 (vs), 1921 (s); ^1H NMR (C_6D_6, 400.1 MHz) δ −9.06 (s, 1 H, ReH), 4.36 (s, 5 H, Cp), 5.65 (s, 1 H, SiH, ^1J(SiH) 182.4 Hz, ^2J(SiSiH) 8.6 Hz), 7.08–7.75 (m, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz) δ 86.06 (Cp), 127.90, 128.19, 135.65, 136.41, 136.61, 141.74 (C_6H_5), 199.55 (CO); $^{29}Si\{^1H\}$ NMR (C_6D_6, 79.5 MHz) δ −25.64 (SiH), −19.09 (ReSi). *Anal.* Found: C, 54.97; H, 4.08. Calc. for $C_{31}H_{27}O_2ReSi_2$ (673.7): C, 55.25; H, 4.04%.

3b: 814 mg (2.4 mmol) of $CpRe(CO)_3$ and 1.18 g (4.9 mmol) of HMePhSi–SiMePhH (mixture of diastereomers). Pale yellow oil; yield 231 mg (17%). IR (Et_2O) ν(CO) 1994 (vs, br), 1932 (s, br). The diastereomers were formed in a 10:9 ratio (by integration of the ^1H NMR signals). Diastereomer A (major diastereomer): ^1H NMR (C_6D_6, 400.1 MHz) δ −9.55 (s, 1 H, ReH), 0.49 (d, 3 H, $Si(C\mathit{H}_3)H$, ^3J(HCSiH) 4.3 Hz), 0.98 (s, 3 H, $ReSiC\mathit{H}_3$), 4.35 (s, 5 H, Cp), 4.81 (q, 1 H, SiH, ^3J(HSiCH) 4.3 Hz), 7.01–7.60 (m, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz) δ −6.49 ($ReSi\mathit{C}H_3$), 3.43 ($Si(\mathit{C}H_3)H$), 85.49 (C_5H_5), 127.84, 128.11, 128.63, 128.94, 135.34, 137.61, 143.45 (C_6H_5), 199.92 (CO); $^{29}Si\{^1H\}$ NMR (C_6D_6, 79.5 MHz) δ −24.97 (SiH), −24.73 (ReSi). Diastereomer B (minor diastereomer): ^1H NMR (C_6D_6, 400.1 MHz) δ −9.56 (s, 1 H, ReH), 0.52 (d, 3 H, $Si(CH_3)H$, ^3J(HCSiH) 4.5 Hz), 1.01 (s, 3 H, $ReSiCH_3$), 4.34 (s, 5 H, Cp), 4.83 (q, 1 H, SiH,

^3J(HSiCH) 4.5 Hz), 7.01–7.60 (m, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz) δ −6.40 ($ReSiCH_3$), 3.68 ($Si(CH_3)H$), 85.51 (Cp), 127.86, 128.14, 128.54, 128.91, 134.72, 135.36, 137.42, 143.53 (C_6H_5), 200.05 (CO); $^{29}Si\{^1H\}$ NMR (C_6D_6, 79.5 MHz) δ −24.92 (SiH), −24.66 (ReSi).

3c: 870 mg (2.6 mmol) of $CpRe(CO)_3$ and 2.0 g (7.8 mmol) of $HPh_2SiSiMe_3$. Colourless solid; yield 221 mg (15%), m.p. 83°C (dec.). IR (Et_2O) ν(CO) 1990 (vs), 1913 (s); ^1H NMR (C_6D_6, 250.1 MHz) δ −9.29 (s, 1 H, ReH), 0.37 (s, 9 H, $SiCH_3$), 4.50 (s, 5 H, Cp), 7.26–7.75 (m, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz) δ −0.51 ($SiCH_3$), 86.18 (Cp), 127.76, 128.23, 136.00, 142.84 (C_6H_5), 200.18 (CO); $^{29}Si\{^1H\}$ NMR (C_6D_6, 49.5 MHz) δ −17.22 ($SiCH_3$), −10.08 (ReSi). *Anal.* Found: C, 46.31; H, 4.02. Calc. for $C_{22}H_{25}O_2ReSi_2$ (563.8): C, 46.87; H, 4.47%.

The dihydride complex **4** was isolated from the reaction with $HPh_2SiSiPh_2H$. After elution of **3a**, the column was washed with CH_2Cl_2. The solvent was then removed in vacuo from the eluted solution and the resulting brown oil chromatographed on silica at 0°C with petroleum ether–CH_2Cl_2 (1:1). The yellow zone was eluted and concentrated to 1 ml. After addition of 2 ml of pentane, **4** precipitated at −78°C as a yellow solid. Yield 86 mg (9%). IR (CH_2Cl_2) ν(CO) 1891 (s), 1952 (s); ^1H NMR (C_6D_6, 250.1 MHz) δ −6.97 (s, 1 H, ReH), 4.69 (s, 5 H, Cp); $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz) δ 84.00 (Cp), 202.26 (CO). *Anal.* Found: C, 27.11; H, 1.94. Calc. for $C_{14}H_{12}O_4Re_2$ (616.3): C, 27.28; H, 1.96%.

4.9. Reaction of $CpRe(CO)_2(THF)$ with HMe_2Si–$SiMe_2H$

$CpRe(CO)_2(THF)$ was prepared as described above from 535 mg (1.6 mmol) of $CpRe(CO)_3$ in 120 ml THF at 4°C. After irradiation, the solution was concentrated in vacuo to about 40 ml, and 370 mg (3.2 mmol) of HMe_2Si–$SiMe_2H$ were added. The solution was refluxed for 1 h. The IR spectrum showed two broad bands at 1985 and 1913 cm^{-1}. The solvent was removed in vacuo after filtration over celite. The resulting brown oil was chromatographed at 0°C on silica with petroleum ether–Et_2O (20:1). The fractions containing the carbonyl compounds were collected (there was no separation of the three products) and investigated by NMR spectroscopy. The signals of the products were assigned according to their intensity (due to the different concentrations of the three products).

3d: ^1H NMR (C_6D_6, 250.1 MHz) δ −10.05 (s, 1 H, ReH), 0.25 (d, 6 H, $SiMe_2H$, ^3J(HCSiH) 4.5 Hz), 0.69 (s, 6 H, $ReSiMe_2$), 4.05 (sept, 1 H, Si*H*, ^3J(HSiCH) 4.5 Hz), 4.52 (s, 5 H, Cp); $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz) δ −5.06 ($ReSiMe_2$), 5.18 ($SiMe_2H$), 85.07 (Cp), 200.17 (CO).

3d′: ^1H NMR (C_6D_6, 250.1 MHz) δ −9.97 (s, 1 H, ReH), 0.17 (d, 6 H, $SiMe_2H$, ^3J(HCSiH) 4.5 Hz), 0.73 (s, 6 H, $ReSiMe_2$), 4.13 (sept, 1 H, Si*H*, ^3J(HSiCH) 4.5 Hz), 4.52 (s, 5 H, Cp); $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz) δ −5.61 ($ReSiMe_2$), 6.33 ($SiMe_2H$), 84.99 (Cp), 200.47 (CO).

5: ^1H NMR (C_6D_6, 250.1 MHz) δ −10.76 (s, 1 H, ReH), 0.73 (d, 6 H, $SiMe_2$), 4.50 (s, 5 H, Cp); $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz) δ 1.93 ($SiMe_2$), 84.43 (Cp), 202.16 (CO).

4.10. Preparation of $(PPh_3)_2(CO)_2Fe(H)_2$ (6)

A solution of 502 mg (1.3 mmol) of $Fe(CO)_4PPh_3$ and 310 mg (2.6 mmol) of HMe_2Si–$SiMe_2H$ in 100 ml petroleum ether was irradiated at 0°C until the ν(CO) bands of $Fe(CO)_4PPh_3$ had disappeared. The solvent is then removed in vacuo and the resulting brown oil dissolved in 30 ml of toluene. The solution was filtered over celite, concentrated in vacuo to 5 ml, and 10 ml of petroleum ether was added. A beige solid precipitated at −78°C, which is dried in vacuo. IR (CH_2Cl_2) ν(CO) 1988 (s), 1950 (s); ^1H NMR ($CDCl_3$, 250.1 MHz) δ −9.24 (t, 2 H, ^2J(PFeH) 58.6 Hz, FeH), 7.39–7.58 (m, 30 H, C_6H_5); ^{31}P NMR ($CDCl_3$, 101.3 MHz) δ 81.36 (t, ^2J(PFeH) 58.6 Hz).

4.11. Preparation of mer-$(CO)_3(PPh_3)Fe(H)SiPh_2SiPh_2H$ (7a)

The solution of 353 mg (0.7 mmol) of $(CO)_3(PPh_3)$-$Fe(H)SiMe_3$ and 272 mg (0.7 mmol) of HPh_2Si–$SiPh_2H$ in 15 ml toluene was stirred for 20 h at 35°C. From the clear, brown solution the solvent was then removed in vacuo. The residual brown oil was three times washed with 10 ml of pentane each. Beige powder, yield 446 mg (78%), m.p. 87°C (dec). IR (petroleum ether) ν(CO) 2035 (m), 1980 (s), 1965 (s); ^1H NMR (C_6D_6, 250.1 MHz) δ −8.42 (d, 1 H, ^2J(PFeH) 25.6 Hz, FeH), 6.02 (s, 1 H, SiH), 7.01–8.22 (m, 35 H, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz) δ 129.11–142.24 (C_6H_5), 211.48 (d, ^2J(PFeC) 12.5 Hz, CO); $^{29}Si\{^1H\}$ NMR (C_6D_6, 49.5 MHz) δ −26.27 (s, $SiPh_2H$), 9.60 (d, ^2J(SiFeP) 10.17 Hz, FeSi); $^{31}P\{^1H\}$ NMR (C_6D_6, 101.3 MHz) δ 62.43. *Anal.* Found: C, 69.84; H, 4.90. Calc. for $C_{45}H_{37}O_3FePSi_2$ (768.8): C, 70.31; H, 4.86%.

When the reaction was carried out in Et_2O instead of toluene, considerable amounts of $(CO)_3Fe(PPh_3)_2$ were formed as a byproduct.

4.12. Preparation of mer-$(CO)_3(PPh_3)Fe(H)SiMePh$-$SiMePhH$ (7b)

The solution of 496 mg (1.0 mmol) of $(CO)_3(PPh_3)$-$Fe(H)SiMe_3$ and 264 mg (1.1 mmol) of HMePhSi–Si-MePhH in 20 ml Et_2O were heated to 35°C for 22 h. The solvent was then removed in vacuo and the resulting brown oil chromatographed on silica at 0°C with petroleum ether–Et_2O (4:1). A yellow fraction containing $(CO)_3Fe(PPh_3)_2$ was first separated. Several fractions were then taken and monitored by ^{31}P NMR spectroscopy. The fractions carrying **7b** were combined and the solvent removed in vacuo. Colourless oil, yield 523 mg (78%). IR (petroleum ether) ν(CO) 2030 (m), 1975 (s), 1965 (s). The diastereomers were formed in a 10:9 ratio (by integration of the ^{1}H NMR signals). Diastereomer A (major diastereomer): ^{1}H NMR (C_6D_6, 250.1 MHz) δ −8.75 (d, 1 H, ^2J(PFeH) 25.6 Hz, FeH), 0.84 (d, 3 H, ^3J(HCSiH) 3.7 Hz, Si(CH_3)H), 1.19 (s, 3 H, $FeSiCH_3$), 5.18–5.20 (m, 1 H, SiH), 7.03–8.06 (m, 25 H, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz) δ −6.65 ($FeSiCH_3$), 2.25 ($Si(CH_3)H$), 127.96–144.38 (m, C_6H_5), 211.90 (d, ^2J(CFeP) 12.5 Hz, CO); $^{29}Si\{^1H\}$ NMR (C_6D_6, 49.7 MHz) δ −28.42 (s, SiH), 2.71 (d, ^2J(SiFeP) 7.6 Hz, FeSi). $^{31}P\{^1H\}$ NMR (C_6D_6, 101.3 MHz) δ 62.20. Diastereomer B (minor diastereomer): ^{1}H NMR (C_6D_6, 250.1 MHz) δ −8.77 (d, 1 H, ^2J(HFeP) 25.6 Hz, FeH), 0.72 (d, 3 H, ^3J(HCSiH) 3.7 Hz, Si(CH_3)H), 1.19 (s, 3 H, $FeSiCH_3$), 5.18–5.20 (m, 1 H, SiH), 7.03–8.06 (m, 25 H, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz) δ −6.32 ($FeSiCH_3$), 2.30 ($Si(CH_3)H$), 127.96–144.45 (C_6H_5), 211.82 (d, ^2J(CFeP) 12.5 Hz, CO); $^{29}Si\{^1H\}$ NMR (C_6D_6, 47.9 MHz) δ −26.89 (SiH), 2.56 (d, ^2J(SiFeP) 7.6 Hz, FeSi). $^{31}P\{^1H\}$ NMR (C_6D_6, 101.3 MHz) δ 62.28.

4.13. Preparation of mer-$(CO)_3(PPh_3)Fe(H)SiPh_2SiMe_3$ (7c)

The solution of 340 mg (0.7 mmol) of $(CO)_3(PPh_3)Fe(H)SiMe_3$ and 183 mg (0.7 mmol) of $HPh_2Si–SiMe_3$ in 20 ml Et_2O was heated to 35°C for 16 h. The solvent was then removed in vacuo and the resulting beige oil chromatographed on silica at 25°C with petroleum ether–Et_2O (2:1). A yellow fraction containing $(CO)_3Fe(PPh_3)_2$ was separated and then the beige fraction carrying **7b** collected. The solvent was then removed in vacuo. Beige powder, yield 382 mg (83%), m.p. 83°C (dec). IR (petroleum ether) ν(CO) 2030 (m), 1980 (s), 1965 (s). ^{1}H NMR (C_6D_6, 250.1 MHz) δ −8.56 (d, 1 H, ^2J(PFeH) 26.9 Hz, FeH), 0.54 (s, 9 H, $SiCH_3$), 7.01–8.11 (m, 25 H, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz) δ 0.09 ($SiCH_3$), 128.74–143.00 (C_6H_5), 212.22 (d, ^2J(PFeC) 12.5 Hz, CO); $^{29}Si\{^1H\}$ NMR (C_6D_6, 49.7 MHz) δ −11.74 (s, $SiCH_3$), 9.31 (d, ^2J(SiFeP) 8.0 Hz, FeSi); $^{31}P\{^1H\}$ NMR (C_6D_6, 101.3 MHz) δ 62.59. *Anal.* Found: C, 66.37; H, 5.51. Calc. for $C_{36}H_{35}O_3FePSi_2$ (658.7): C, 65.64; H, 5.36%.

When the reaction was carried out in toluene instead of ether, $(CO)_3Fe(PPh_3)_2$ and **7c** were formed in a 1:1 ratio. Reaction in petroleum ether at 40°C was much slower, and **7c** was only formed as a byproduct, the main product being $(CO)_3Fe(PPh_3)_2$.

4.14. Reaction of of mer-$(CO)_3(PPh_3)Fe(H)SiMe_3$ with $HMe_2Si–SiMe_2H$

A solution of 210 mg (0.4 mmol) of $(CO)_3(PPh_3)Fe(H)SiMe_3$ and 104 mg (0.9 mmol) of $HMe_2Si–SiMe_2H$ in 20 ml of toluene was stirred at 25°C. The reaction was monitored by ^{31}P NMR spectroscopy. After 26 h the spectrum showed weak signals of $(CO)_4Fe(PPh_3)$ and $(CO)_3Fe(PPh_3)_2$, and the signals of **8**, **7d**, and $(CO)_3(PPh_3)Fe(H)SiMe_3$ in a 2:6:1 ratio. After 5 days the signals of $(CO)_3(PPh_3)Fe(H)SiMe_3$ and **7d** had disappeared, and only those of **8** were observed.

Spectroscopic data of **7d**: ^{1}H NMR (C_6D_6, 250.1 MHz) δ −8.88 (d, 1 H, ^2J(PFeH) 25.6 Hz, FeH), 0.49 (d, 6 H, ^3J(HCSiH) 3.7 Hz, $Si(CH_3)_2H$), 0.94 (s, 6 H, $FeSiCH_3$), 4.43 (sept, 1 H, ^3J(HSiCH) 3.7 Hz, SiH), 7.04–7.61 (m, 15 H, C_6H_5); $^{31}P\{^1H\}$ NMR (C_6D_6, 101.3 MHz) δ 62.20.

Spectroscopic data of **8**: IR (petroleum ether) ν(CO) 2030 (m), 1980 (s), 1965 (s); ^{1}H NMR (C_6D_6, 250.1 MHz) δ −8.30 (d, 1 H, ^2J(PFeH) 26.8 Hz, FeH), 1.26 (s, 6 H, $SiCH_3$), 7.05–8.01 (m, 15 H, C_6H_5); $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz) δ 4.75 ($SiCH_3$), 127.41–136.47 (C_6H_5), 212.74 (d, ^2J(PFeC) 10.4 Hz, CO); $^{31}P\{^1H\}$ NMR (C_6D_6, 101.3 MHz) δ 62.98. $^{29}Si\{^1H\}$ NMR (C_6D_6, 49.7 MHz) δ 19.57.

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